INORGANIC CHEMISTRY

FOR

BEGINNERS

BY

SIR HENRY ROSCOE, F.R.S., D.C.L., LL.D.,

ASSISTED BY

JOSEPH LUNT, B.Sc. (Vict.), F.C.S.

ASSISTANT EXAMINER IN CHEMISTRY TO THE SCIENCE AND ART DEPARTMENT.

With One hundred and eight Illustrations in the Text

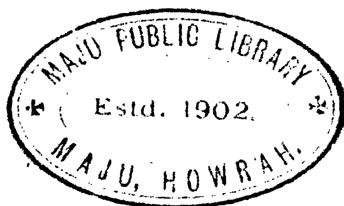
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PREFACE

THE publishers of the Elementary Lessons in Chemistry have brought before my notice the want of a work for those beginning the study of the science, in which the elementary principles of chemistry are more fully treated than is the case in the Lessons, whilst the description of the elements and their compounds is restricted to a few well-chosen typical examples. In the present pages I have endeavoured to fulfil the above requirements, and I have found no selection more suitable to the needs of beginners than that made many years ago for this purpose, and still found to be effective, by the Department of Science and Art. It will be seen that whilst the ground covered in this little book is confined to the discussion of a portion only of the non-metallic elements, a greater amount of detail is in each case given than was found to be possible in the Lessons.

H. E. R.

August 1893.

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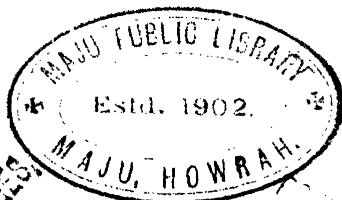
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PART I

ELEMENTARY PRINCIPLES

LESSON I

SOLIDS, LIQUIDS, AND GASES*

THE existence of different kinds of solids, such as wood and iron, and of different kinds of liquids, such as oil and water, has been recognised by men from the very earliest times ; but that similar differences exist amongst invisible gases has only been ascertained within a comparatively recent period. These differences can, however, be readily shown by experiment.

EXPT. 1. **Behaviour of different Gases towards a burning Taper.** — Here, for example, are three bottles filled with colourless invisible gases. I remove the stopper and plunge a lighted taper into the first one, and we observe that it is at once extinguished. I put the burning taper into the second vessel, when we notice that it burns with very much increased brilliancy ; and if I bring it to the mouth of the third vessel, we find that the gas takes fire and burns with a pale blue flame.

EXPT. 2. **Heavy and Light Gases.**—Not only do these three gases differ essentially from one another, in their behaviour towards a burning taper, as we have seen, but they also differ greatly in weight. Thus, if we take three bottles

* A *solid* body has a definite form, and tends to keep it ; a *liquid* body must be kept in a vessel, and adapts itself to the shape of that vessel, but so as to keep its upper surface horizontal, it tends moreover to flow from a higher to a lower level. A *gas* or a gaseous body cannot be kept in an open vessel, but must be kept in a vessel closed in on all sides, it always fills the vessel completely. Liquids and gases are both called fluids.

of the same three gases, and in the same order, we can easily prove that the first not only puts out a taper, but is a very heavy gas and may be poured *downwards* from one vessel to another like water. Although we cannot see the gas pour from one vessel to another, it is easy to show that it has passed from B to A (Fig. 1), by means of a lighted taper, for the flame is put out in A, into which the heavy gas has been poured, whilst it burns quite well in B, which at first contained the heavy gas, but which now contains ordinary air that enters as the heavy gas leaves. In the same way we can show that the third vessel contains a very light gas. This time we shall be able to pour it *upwards* (see Fig. 2). Having inverted the gas jar B, I take

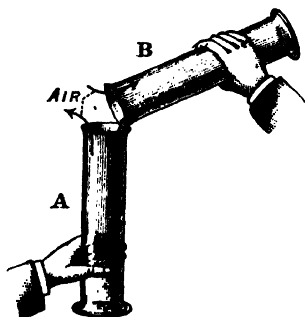


Fig. 1.

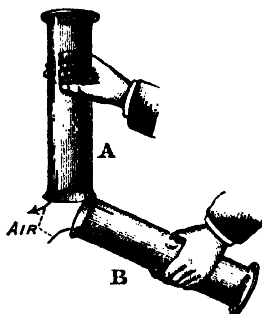


Fig. 2.

off the cover and apply its mouth to the mouth of A, also inverted, and gradually lower the upper end of B, so as to pour the gas upwards into A. As the light gas ascends into A, the air is driven out, and as the gas leaves B, its place is taken by ordinary air. This is easily seen to be the case by applying a lighted taper to the mouth of both jars; A is now seen to contain the inflammable gas, because it takes fire, whilst in B the taper burns just as in ordinary air.

EXPT. 3. **Heavy and Light Gases in the Balance.**—Another method of proving that there are heavy and light gases may be shown as follows. At the two ends of the arms of a balance are fixed two thin beaker-glasses (Fig. 3), one inverted and the other not. These are exactly balanced

when both are filled with air, by adding a little sand to the lighter end. If now we have three more bottles of the different gases, and pour the contents of the first one downwards into beaker A, we see that the heavy gas weighs it down and the beaker descends although nothing can be seen to have entered the beaker. In the same way if we again equipoise the vessels, the contents of our third jar, poured upwards into B, (Fig. 4), make it ascend, showing it to be filled with a very

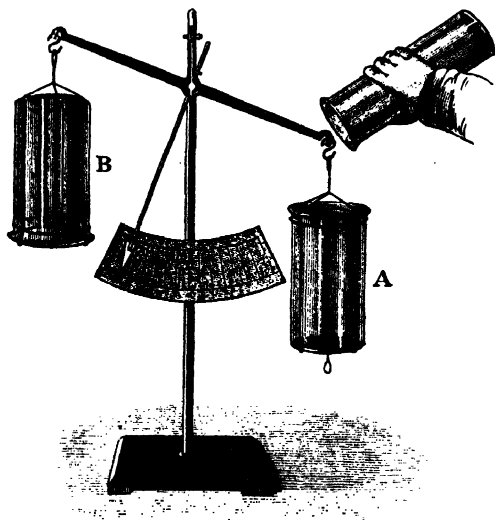


Fig. 3.

light gas. Whilst our second gas, if we empty the beakers of the first gases and put them again in equilibrium, will be found neither to weigh down A nor raise B, because it is just about as heavy as ordinary air.

EXPT. 4. **Behaviour of Gases towards Lime-Water.** —Again, if we take some clear lime-water * and pour it into jars of the three gases used in the first experiment, we find that in the first one it becomes quite white and milky, whilst in the

* See footnote to p. 139.

two others it does not do so. This is because the first gas forms with the lime in the lime-water a white substance almost exactly like chalk, which floats about in the water and turns it milky. The other two gases do not form this white substance with lime-water and produce no change in it.

These, then, are simple examples of the *experimental method* which the chemist uses, and it is by experimenting that the

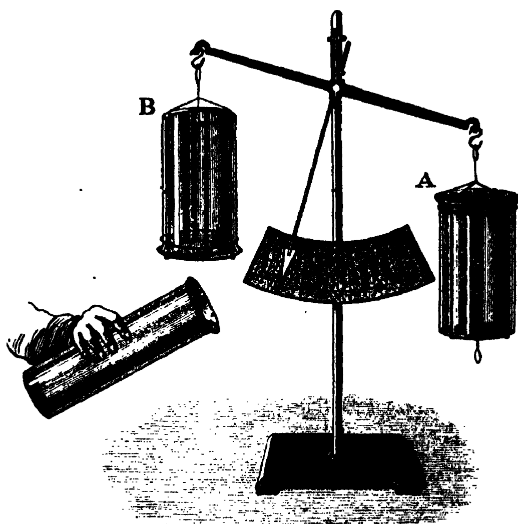


Fig. 4.

chemist has been able to find out all that he knows about the different materials of which Earth, Air, and Water are made up.

EXPT. 5. **Substances can exist in any of the three States. Water.**—We now see that every substance may be classified as either solid, liquid, or gas; but it will be evident, after a little consideration, that many substances can exist in more than one of these forms. Let us take the familiar example of water. If we place a saucer full of water out in the air in winter when it is freezing, we see that the water is turned

into solid ice. Yet if this be brought into a warm room the ice melts, and we again get liquid water, whilst if we pour this into the kettle and put it on the fire, we soon get the water in the state of gas or steam, which, just as it rushes out of the spout of the kettle, is quite invisible, but a little way from the spout is seen as a cloud or mist consisting of very small drops of liquid water.

EXPT. 6. **Gaseous Water or Steam invisible.**—That the true steam (or gaseous water) is invisible, is easily shown by boiling the water in a glass flask fitted with a cork and bent tube, as in Fig. 5. When the water boils, the cloud of condensed steam is seen to rush out from the little glass tube, but inside the flask, above the boiling water, nothing can be seen, but still the space must be full of gaseous water, for directly it gets into the cold air it becomes condensed into a cloud of minute particles of liquid water. Water, then, exists in the solid state, as ice, snow, and hail; in the liquid state as water; and in the gaseous state as steam.

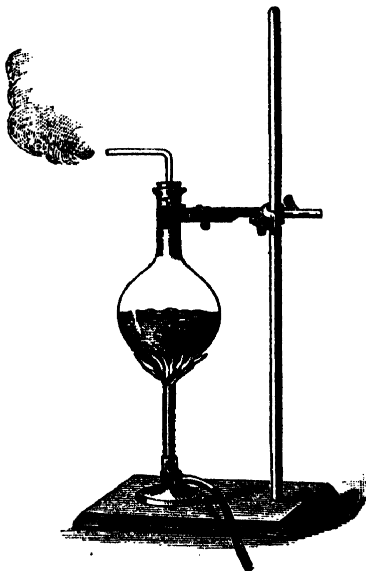


Fig. 5.

EXPT. 7. **Sulphur as a Solid, Liquid, or Gas.**—In the same way Sulphur, a yellow solid body, if heated in a glass retort, will first melt to a liquid, and if this be heated still further, it will give off a very dark-red gas which condenses in the cold neck of the retort to liquid, and then to solid sulphur.*

EXPT. 8. **Iodine in the Gaseous State.**—Similarly the black metallic-looking substance Iodine, if dropped into a hot flask, immediately fills it with a beautiful violet gas, which, as

* Fig. 94 shows the method of heating a substance in a retort.

it cools, condenses on the sides of the flask as a sparkling mass of black crystals.

Even the liquid metal mercury can be made to assume the gaseous state by strongly heating it in a glass retort. The gaseous metal passes into the neck of the retort and is there cooled and condensed to shining little drops of quicksilver, which run into the small flask placed to receive them. If these be put in a freezing mixture which produces *intense* cold, the liquid metal becomes solid and can be hammered or moulded into various shapes like a piece of lead. Most solid substances, if heated strongly enough, unless they decompose, will melt to a liquid, and liquids, if heated strongly enough, will boil and become gaseous. Similarly, all gases will condense to liquids, and all liquids, if they are made cold enough, will assume the solid state. Some gases are easily condensed to liquids, such as steam, whilst others require to be cooled to a point far colder than ice or even than the coldest Arctic winter, and, moreover, must at the same time be subjected to very great pressure, before they condense to liquids. Similarly with liquids, some are easily solidified, such as water, whilst others must be cooled down to a very low point before they solidify. We must, however, remember that in all these transformations of solid into liquid, and of liquid into gas, and *vice versâ*, the essential nature or *chemical composition* of the substances is not altered, they are merely *physical* changes. On the other hand, whenever a *chemical change* takes place, the essential nature or *chemical composition* of the substance or substances undergoing the change becomes altered, and in this way we can distinguish between a *physical* change and a *chemical* change. In our next lesson we shall have many examples of the latter. A piece of iron may become magnetised by an electric current, or a platinum wire may be heated to whiteness by the same means, or a piece of glass may be electrified by friction. These are merely *physical* changes.

WHAT WE HAVE LEARNT

In our first Lesson we have learnt that not only are there different kinds of solids and liquids, but also different kinds of gases, which, although quite colourless and invisible, may be shown to be different by means of suitable experiments, such as that with a burning taper or by that of pouring them from one vessel to another, or of weighing them on a balance. The three gases considered are (1) a very heavy gas, which puts out the flame of a burning taper and turns lime-water milky. This is called Carbonic Acid Gas. (2) A very light gas which burns in air with a blue flame and does not turn lime-water milky. This is called Hydrogen. (3) A gas just about as heavy as ordinary air, in which the taper burns with greatly increased brilliancy, and which does not turn lime-water milky. This is called Oxygen. We have also learnt that many substances, such as water, sulphur, iodine, and mercury, can exist in any of the three states of matter, *e.g.* water, as solid ice, snow, and hail; as liquid water, and as gaseous steam. Similarly, gases may be condensed to liquids and liquids to solids without altering their chemical composition.

EXERCISES ON LESSON I

1. How can you distinguish oxygen from hydrogen, and carbonic acid from either?
2. Mention several solids, liquids, and gases.
3. How can you show that gaseous water is invisible?
4. What happens when iodine is heated in a glass flask?
5. Describe any experiments which show that there are different kinds of colourless invisible gases.
6. What happens when lime-water is poured into (1) oxygen, (2) hydrogen, (3) carbonic acid gas?
7. What is meant when we say that water can exist in any of the three states of matter?
8. What happens when a burning taper is placed in (1) oxygen, (2) hydrogen, (3) carbonic acid?
9. How can you show by experiment that hydrogen is a light gas and carbonic acid gas a heavy gas?

LESSON II

THE AIR, INTRODUCTORY

LET us now try to find out something about the very commonest gas with which we are acquainted, namely, the atmosphere or air which surrounds us.

EXPT. 9. **Burning Phosphorus in Air; the Air contains two Gases.**—Let us take a large glass bell-jar A, furnished with a stopper at its neck, and place it over water in a glass dish B, so as to enclose air inside the bell-jar (Fig. 6), the water rising to the level of the first mark, so as to enclose five volumes of air. We will float on the water a small porcelain dish D in which a small piece of dry phosphorus* has been placed. Taking out the stopper of the jar and introducing a glass rod, the end of which has been heated in a gas flame, I will touch the small piece of phosphorus with it, and this being very inflammable immediately takes fire and burns with a bright white light. Quickly replacing the stopper we see that the jar becomes filled with dense white fumes, and that after a time the phosphorus begins to burn dimly and soon afterwards the flame dies out. Then the dense white

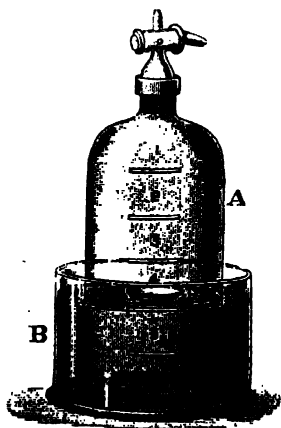


Fig. 6.

* Phosphorus must always be cut under water, and must not be handled by warm fingers.

fumes begin to dissolve in the water and disappear. When the gas inside has cooled down to the ordinary temperature of the air, I pour water into the glass trough until the water both inside and outside the bell-jar is at the same level (Fig. 6). It will now be seen that we have less gas in our bell-jar than when we started the experiment; and if we exactly measure the amount or volume of air we begin with, we shall find that we have just about $\frac{4}{5}$ of the original volume left, for the water has now risen to the second mark on the bell-jar, showing that the original five volumes have become four volumes.

Now let us see how the gas remaining will behave towards a burning taper. On removing the stopper and plunging in the lighted taper the flame will at once be extinguished. Evidently the gas remaining in the bell-jar after phosphorus has been burnt in it is something different from ordinary air, because in ordinary air a taper will burn, but in this gas it will not. (This gas is called **Nitrogen.**) Perhaps that may have been the reason why the light of the phosphorus was put out. Let us see if that is so. On taking out the stopper and removing the bell-jar from the glass trough we shall find, if we have taken sufficient phosphorus, that it again bursts into flame in ordinary air if touched with a hot glass rod, showing that the flame of the phosphorus did not go out because all the phosphorus had been burnt away and used up, but rather because something in the air which allows things to burn has been used up, and $\frac{1}{5}$ the volume of the air consists of this gas which is used up when phosphorus burns in it.

EXPT. 10. **Lavoisier's Experiments on Air.**—We will now try to find out something more about the air with which we are surrounded. We know already that $\frac{4}{5}$ of it is composed of nitrogen, which does not allow things to bu in it. What is the other $\frac{1}{5}$ composed of? To find t out, I will describe an experiment which was made a lon time ago by the French chemist Lavoisier. Into a glass balloon or retort A, having a long straight neck, Lavoisier brought a few ounces of dry mercury or quicksilver; he then bent the neck so that when the balloon rested over the flame B, the end of the neck appeared above the surface of the mercury contained in the large glass dish C (Fig. 7). Thus the air enclosed in the bell-jar D was in communication with that

in the retort. The volume of air contained in the bell-jar and retort was first measured, and then the mercury in the retort was made very hot by a flame placed underneath. For the first few hours no change occurred, but then red-coloured specks and scales began to make their appearance. These increased in number for some time, but subsequently no further formation of this red substance was observed; so after the experiment had been continued for twelve days the fire was removed and the volume of the air was seen

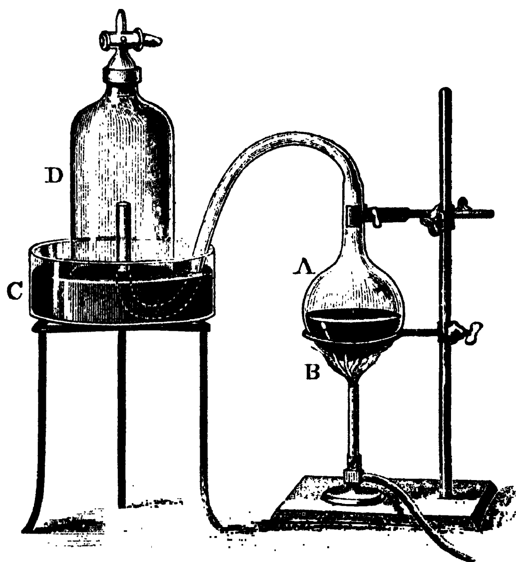


Fig. 7.

to have undergone a remarkable diminution, which when measured was found, just as in our experiment with the phosphorus, to be about $\frac{1}{5}$ of the original volume. Where has this $\frac{1}{5}$ of the air gone to? It has burnt up a small portion of the mercury in the retort and formed the red powder on its surface, and this red powder contains the part of the air ($\frac{1}{5}$ of its original volume) which is consumed in burning (either a taper or a fire or anything else). Lavoisier next very carefully collected all the red powder and placed it

in a long tube (Fig. 8), connected with a graduated glass cylinder. On heating the red powder very strongly he found that it gave off exactly the same volume of gas which had disappeared in the previous experiment, and on testing it, found it to be the gas in which things burn so readily (this is called **Oxygen**).* This gas is therefore termed a *supporter of combustion.* That oxygen does support combustion most powerfully is shown by introducing a chip of wood with only the least spark on it into the gas, when the wood will im-

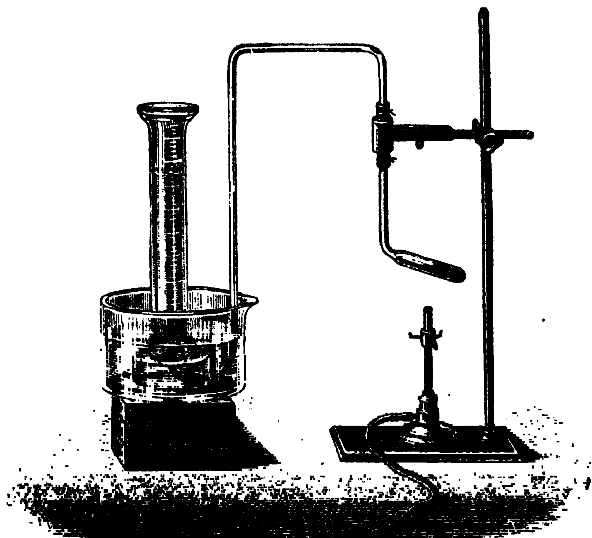


Fig. 8.

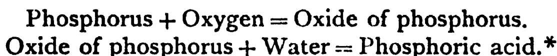
mediately burst into bright flame. This is a *test* for oxygen gas.

Let us now consider the meaning of these experiments a little more closely.

In the first experiment (Expt. 9) we burnt phosphorus in air, and we now know that the air contains oxygen and nitrogen. When phosphorus burns, it is *combining* chemically with

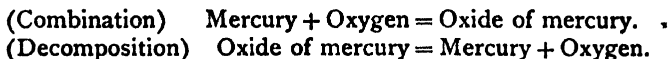
* Priestley had previously prepared oxygen by heating mercuric oxide (see p. 74).

oxygen, and during this *chemical action* heat and light are evolved. In very many cases of chemical action we shall find that heat and sometimes light is given off. Here we have a good example of *chemical combination;* the yellowish wax-like solid combines with the oxygen gas to form the white solid called oxide of phosphorus, the fumes of which filled our bell-jar. We notice here that in this chemical combination two different substances have united chemically to form a third substance differing entirely in its properties from the materials of which it is made up. We next notice that the fumes of the white solid oxide of phosphorus soon disappear, and that is because another chemical action takes place. The oxide of phosphorus unites chemically with the water in the glass dish, and forms a substance which dissolves in the water; this is called phosphoric acid. That the water in the trough contains a new substance may be shown by pouring into it a little blue litmus solution, which immediately turns red, proving that an acid is present. This is a *test* for an acid. Thus we have


Phosphorus + Oxygen = Oxide of phosphorus.
Oxide of phosphorus + Water = Phosphoric acid.*

The nitrogen present in the air takes no part in these *chemical reactions.*

Now let us further consider the results of Expt. 10. In the first part we have another example of chemical combination. The silvery liquid mercury, or quicksilver, unites chemically with the oxygen of the air and forms a red powder called oxide of mercury. In the second part, the oxide of mercury is chemically decomposed, yielding mercury and oxygen. This is an example of *chemical decomposition*, and we notice that one substance in decomposing yields two entirely different substances. The powder is a red solid, and its products of decomposition are a silvery liquid and a colourless gas. Thus we have:


(Combination) Mercury + Oxygen = Oxide of mercury.
(Decomposition) Oxide of mercury = Mercury + Oxygen.

* The sign + is here used to signify "and," or "together with," whilst the sign = means "yields." We shall afterwards find that these signs may mean more than I now need explain.

In this case we notice that mercury and oxygen must be raised to a high temperature before they will combine, whilst at a *still higher* temperature the oxide of mercury decomposes.

Meaning of Analysis and Synthesis.—When mercury and oxygen combine together, a *synthesis* (joining together) of mercuric oxide from its elements is said to take place. When mercuric oxide is decomposed by heat it is said to be an *analysis* (or splitting asunder) of that compound.

WHAT WE HAVE LEARNT

In our second Lesson we have burnt phosphorus in air enclosed in a bell-jar, and noticed that the volume of air is diminished by $\frac{1}{5}$, leaving $\frac{4}{5}$ of a gas called nitrogen which puts out a burning taper (but which will not turn lime-water milky, distinguishing it from carbonic acid). During the burning, the phosphorus is combining chemically with the oxygen of the air, forming oxide of phosphorus, which combines with the water to form phosphoric acid, a substance which turns blue litmus solution red. Lavoisier's experiment shows us that the $\frac{1}{5}$ of the original air which disappears, combines with mercury to form a red solid, called oxide of mercury; this, on heating strongly, gives off the oxygen which it contains, and this gas is seen to occupy a volume equal to that which was lost in the first instance. The gas oxygen is in this manner separated from the nitrogen, and we find that air is made up principally of nitrogen (four volumes) and oxygen (one volume).

We have had four examples of chemical action, three of chemical combination, viz. (1) phosphorus and oxygen, (2) oxide of phosphorus and water, (3) mercury and oxygen; and one example of chemical decomposition, viz. oxide of mercury into mercury and oxygen.

EXERCISES ON LESSON II

1. Describe an experiment showing that air contains $\frac{4}{5}$ its volume of nitrogen; state some properties of nitrogen.
2. How can you *separate* the oxygen from the nitrogen of the air? How would you *test* for oxygen?
3. What evidence have you that *an acid* is formed when you burn phosphorus in air confined over water? How would you *test* for an acid?
4. Give some examples of chemical combination and decomposition.
5. What is meant by the terms analysis and synthesis?

LESSON III

WATER, INTRODUCTORY—MECHANICAL MIXTURE AND CHEMICAL COMBINATION — INDESTRUCTIBILITY OF MATTER.

THE ancients recognised only four (so-called) elements—Earth, Air, Fire, and Water. We have already seen that the air consists principally of two gaseous substances with widely different properties. Now let us examine another of the so-called elements of the ancients, viz. *water*. Here again we

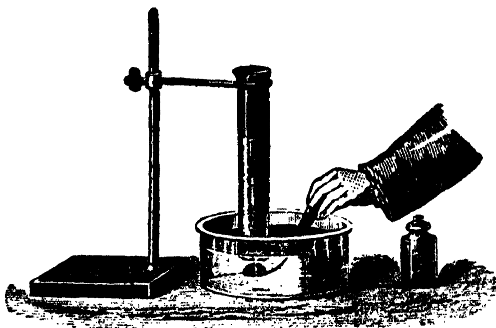


Fig. 9.

will make use of the experimental method of examination which chemists use.

EXPT. 11. **Action of Sodium on Water.**—Here is a small bottle containing the soft white metal sodium, which must always be kept under mineral oil because it is rapidly acted upon by the moisture in the air. If I take a lump of the

sodium and cut off a small piece with a knife (for sodium, although a metal, is very soft and can easily be cut), and then introduce the little piece of sodium into a small wire cage furnished with a handle, and plunge it into a glass dish full of water over which is inverted a gas cylinder also filled with water (Fig. 9), we notice at once a violent action going on, and bubbles of gas rise and fill the gas cylinder placed to receive them. Here the sodium has decomposed the water and driven out or liberated one of its components (which we can recognise as hydrogen if we apply a lighted taper to the gas); whilst the sodium has united or combined with the remaining portion of the water to form a new substance, caustic soda, which remains dissolved. That a new substance is dissolved in the water is easily shown by adding some red litmus solution; it is immediately turned blue. This is a test for alkalis, and caustic soda is an alkali.

Sodium + Water = Caustic soda + Hydrogen.

Evidently then water contains hydrogen. What else does it contain? A further experiment will tell us.

EXPT. 12. **Electrolysis of Water into Oxygen and Hydrogen.**—Here is a battery* which will furnish a current of electricity; this has the power, if passed through various bodies, of decomposing them into their components. In Fig. 10 we see the apparatus which is used for passing a current of electricity through water. The two wires from the battery terminate in platinum plates, and over each one hangs a little glass cylinder filled with acidulated water. Directly we allow the current to pass through, we notice that from each platinum plate small bubbles of gas begin

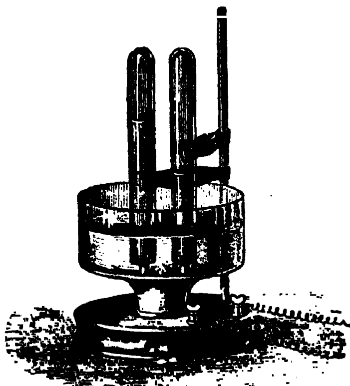


Fig. 10.

* See Fig. 48, p. 95.

to arise, and these pass up into the two tubes placed to receive them, and soon we observe that one tube is filling with gas much faster than the other, and at last, when one of the tubes is quite full the other is only half full. The current of electricity, in passing through the water, has rent its components asunder and separated them one at one pole or electrode * and the other at the opposite one. Let us now ascertain what these gases are. For this purpose we will take the tube, which is full, out of the water, keeping it closed with the thumb all the time, and then try to light the gas with a taper. We see, as in the last experiment, that the gas takes fire and burns with a blue flame, so this is hydrogen. If now we put a glowing chip of wood into the other tube half filled with gas, it immediately bursts into flame, showing that the gas is oxygen. This experiment teaches us that from *water* we can obtain two volumes of hydrogen and one volume of oxygen.

Water = Hydrogen + Oxygen.

The operation of *decomposing* a substance by passing through it a current of electricity is called *electrolysis*.

Let us try to understand more clearly what is meant by chemical combination, and how to distinguish this from a mere mechanical mixture of two bodies.

EXPT. 13. **Sulphur and Iron mechanically mixed and chemically combined.**—A simple experiment will illustrate what this means. I will take a small quantity of fine iron filings, place them in a mortar, and add to them about the same quantity of yellow flour of sulphur ; on rubbing these two together a greenish powder is produced. Examined by the naked eye the separate particles of iron and sulphur cannot be seen ; if, however, we use a magnifying glass, they can be distinguished lying side by side, and by using a small magnet, the iron can be drawn out and the sulphur left behind. Next I place some of this greenish powder in a test-tube, and heat it over a gas flame. We notice that the mass becomes red-hot. Having allowed it to cool, I break the end of the tube in a clean

* The poles or electrodes are the platinum plates in which the two wires from the battery terminate.

mortar; a black solid mass (sulphide of iron) is seen to have been formed, in which the particles of iron and the particles of sulphur cannot be noticed to lie side by side as before, even when viewed by a powerful microscope, nor can I draw out any particles of iron by means of the magnet.

In the first part of the experiment I have made a *mechanical mixture* of the two powders. In the second I have brought about a *chemical combination.* By no mechanical process can the sulphur and the iron then be separated. This, however, can be done by chemical means; and if I could weigh the sulphur and the iron to begin with, and afterwards weigh the black mass, I should find that the weight of the latter is exactly equal to the weight of the original materials which I used.

Matter is Indestructible.—In all the different changes of this sort which chemists have been able to bring about, they have found that if care be taken, the weight of the chemical substances produced is always equal to the weight of the substance or substances before the change. In other words, *matter is indestructible*, and this is true even where an apparent loss of matter takes place. Thus, when a candle burns, the wax of the candle gradually disappears, and of course the weight of the candle as gradually diminishes. A simple experiment, however, shows that the materials of the wax are not *lost* or destroyed but have passed into a state in which we cannot see them, but their existence can easily be shown by the following experiment.

EXPT. 14. **Carbonic Acid Gas produced when a Candle burns.**—I place a burning candle for a few minutes in a clean bottle filled with air. On withdrawing the candle I pour into the bottle some clear lime-water, and notice that this at once becomes milky, which it does not do if I pour some into another bottle filled with air, in which a candle has not been burnt; proving that the invisible gas, carbonic acid, which turns lime-water milky has been formed by the burning of the candle. Some of the wax has been changed, by burning, into carbonic acid gas, a compound of carbon, one of the materials of the wax, with the oxygen of the air. It is easy to show that the white wax contains carbon, for some carbon goes away as soot or smoke when a candle is burnt, and this we notice by

pressing a sheet of white paper quickly on to the flame so as not to burn it, when the paper becomes blackened with soot or carbon.

EXPT. 15. **Water (gaseous) also produced when a Candle burns.**—But besides carbonic acid, water is formed when a candle burns. This is shown by holding a cold dry bright glass, such as a tumbler, over the flame of the taper. The bright glass becomes at once dim, and small drops of water are seen like little drops of dew inside the glass. This is because a candle not only contains carbon but also hydrogen, and this in burning or combining with the oxygen of the air forms water. For just as we were able to obtain oxygen and hydrogen by decomposing water, so by combining oxygen and hydrogen we again obtain water. This water is given off from the candle in the invisible gaseous state as steam, but in coming in contact with the cold glass it is cooled sufficiently to form liquid water. If, then, what I have said is true, namely that when a candle burns a chemical combination takes place between the materials of the candle and oxygen gas, if we could collect the whole of the carbonic acid and the water formed when the candle burns, the weight of these products must be actually greater than the weight of the candle which has disappeared, because oxygen, like every other gas, possesses weight, and the increase of weight which is observed must be exactly equal to the weight of the oxygen which has combined with the carbon and hydrogen of the candle.

EXPT. 16. **No loss of Weight, but an Increase, observed when a Candle burns.**—First, we will take a wide tube (A) ¾ inch wide and 10 inches long, and into the bottom fit a cork which is perforated with holes to admit air, and then fix our candle inside the tube, and resting on the perforated cork. Then to the top of the tube we will fit another cork, through which a piece of glass tubing passes to a U-shaped tube, which is filled with small pieces of a white solid substance called caustic soda, which has the power of combining with and, therefore, absorbing carbonic acid and water. Next, having placed our unlighted candle in position, we will carefully weigh the whole arrangement as shown in Fig. 11 on one arm of a pair of scales.

The tube C is now connected by an india-rubber tube to a perforated cork at the top of a large bottle of water, which has a tap at the bottom for drawing off the water. If we allow the water to run out of our large bottle, air must pass through the perforated cork through the U tube, and fill the upper part of the bottle as the water flows out; whilst, if we light the candle, not only is the flame in this way supplied with the air which is necessary for it to burn, but the invisible gases which are given off are drawn over the small pieces of caustic soda, and the carbonic acid gas and water vapour absorbed, whilst the remainder of the air (nitrogen) passes into the upper part of the bottle. On making the experiment, and again weighing the tubes and their contents, it will be seen that an *increase* in weight has occurred, and that nothing has been lost or destroyed. We can now understand that the burning of a candle is an example of chemical action. In the same way the burning of coal is due to the same chemical combination of the carbon and hydrogen of the coal with the oxygen of the air.

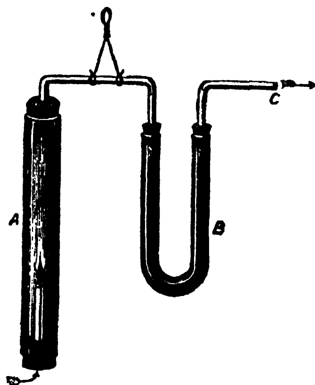


Fig. 11.

What we have learnt

In the third Lesson we have seen that sodium has the power of decomposing water, liberating hydrogen, and forming caustic soda, which turns red litmus blue. Water is decomposed or electrolised into the two gases, oxygen (one vol.) and hydrogen (two vols.), by passing through it a current of electricity from a battery.

We have also learnt the difference between mechanical mixture and chemical combination. We have likewise learnt that in all the changes which the chemist brings about, no loss of matter occurs. He can neither create matter nor destroy it. We have seen how to prove that carbonic acid gas and water are produced when a candle burns, and that no loss, but an actual increase, in weight occurs, owing to the combination of the oxygen of the air with the materials, carbon and hydrogen, of the candle.

Exercises on Lesson III

1. Describe the action of sodium on water.
2. How can you obtain the two gases oxygen and hydrogen from water?
3. Describe fully what happens when a candle burns, and mention any experiments which prove your assertions.
4. Explain the difference between a mechanical mixture of two elements and a chemical compound of the same?
5. What is meant when we say matter is indestructible?
6. How would you demonstrate the presence of (1) an acid, (2) an alkali dissolved in water?
7. Describe an experiment to show that when a candle burns an increase in weight occurs.
8. What is meant by *electrolysis?*
9. Why must sodium always be kept under mineral oil?
10. The ancients considered water to be an element; how can you show that it is not one?

LESSON IV

ELEMENTS AND COMPOUNDS—SYMBOLS AND FORMULÆ—DISTRIBUTION OF THE ELEMENTS

Elements and Compounds.—Having obtained a general idea of what Chemistry means, we will go a little farther into detail, using the knowledge we have already gained to help us to understand some important principles. By experimenting on all kinds of substances, the chemist has found that whether they belong to earth, air, or sea; to the animal, vegetable, or mineral kingdoms, they can be divided into two great classes, namely, *Elements* and *Compounds*.

An element is a substance out of which nothing different has been obtained, or which has not been decomposed into two or more distinct and different substances.

It is quite possible that some of the substances which we now call elements may, by further experiments, be split up into simpler bodies; and such cases have, before now, occurred. The alkalis, potash and soda, were classed as elements until 1807, when Sir Humphry Davy decomposed them and obtained the metals, potassium and sodium.

The elements may be subdivided into metallic elements and non-metallic elements.

A compound is a body formed by the *chemical combination* of two or more elements, and out of which two or more different elements can be obtained. Elements, then, are undecomposible substances, whilst all compounds are decomposible substances from which two or more elements can be separated.

Common Elements, Metals, and Non-metals.*—

	Non-Metals.	Metals (*Solids*).
Gases	Oxygen	Iron
	Hydrogen	Silver
	Nitrogen	Gold
	Chlorine	Lead
Liquid	Bromine	Tin
Solids	Iodine	Zinc
	Carbon	Nickel
	Sulphur	Mercury (*Liquid*)
	Phosphorus	Sodium
	Arsenic	Copper
	Silicon	Aluminium

Occurrence and Distribution of the Elements.— Comparatively few of the elements occur in the free or uncombined state in nature. Amongst these are oxygen and nitrogen; these exist free and mechanically mixed together in the atmosphere. Sulphur occurs in the free state in large deposits in the neighbourhood of volcanoes, especially in Sicily. Carbon occurs free, in its purest natural form, crystallised as the diamond, in Brazil, South Africa, India, and other places. It also occurs naturally in many places as graphite (commonly called black-lead although it contains no lead). Antimony, arsenic, copper, gold, silver, platinum, and mercury also occur in the free state. Iron is also found as large metallic masses in meteoric stones which have fallen to the earth from a source outside our atmosphere; these are seen and usually known as "shooting stars." Although many of the elements occur in the free state in nature, they are more often found in the state of combination with other elements, *e.g.* the metals are usually found in metallic ores combined with one or more of the following elements—sulphur, carbon, oxygen, silicon, chlorine, fluorine, phosphorus, etc.

Hydrogen and oxygen occur combined as water, in addition to being essential constituents of all animal and vegetable bodies. Most organic compounds contain them, often combined also with nitrogen and sulphur. Man has only been able to penetrate a very short distance into the earth's solid crust, even in his deepest mines, so we cannot be certain about the composition of the central portion of our globe.

* A more complete list of the elements is given on p. 32. For an account of the general characters of metals as distinguished from non-metals, see p. 245, Appendix.

The various elements occur scattered very irregularly throughout the earth. Some are very abundant and occur widely distributed, whilst others have been found in such minute quantities, and in such rare fragments, that their properties have not yet been fully studied; *e.g.* oxygen occurs throughout the earth, sea, and air in such quantities as to make up nearly half the weight of the earth's crust.

The following figures show the approximate percentage composition of the granitic rocks, of which the mass of the earth's crust is made up:—

Oxygen . .	44.0 to 48.7	Calcium . .	6.6 to 0.9
Silicon . .	22.8 to 36.2	Magnesium . .	2.7 to 0.1
Aluminium .	9.9 to 6.1	Sodium . .	2.4 to 2.5
Iron . . .	9.6 to 2.4	Potassium . .	1.7 to 3.1

Compounds.—The following are a few examples of compounds: carbonic acid gas, water, alcohol, sugar, caustic soda, oxide of phosphorus, phosphoric acid, oxide of mercury, lime, and chalk.

The compounds formed by the combination of two or more elements are very often markedly different in their appearance and properties from the elements of which they are composed. We have already had some examples of this, and we will now take a few more from the compounds of the metals with non-metals.

EXPT. 17. **Copper in Bluestone.**—Here, for instance, I have some bluestone or blue vitriol, which contains copper, sulphur, and oxygen, although we find no indication of the fact on simply looking at it.

It is easy, however, to prove that it contains *copper*. One has simply to dip one half of a clean steel knife blade in a *solution* of the blue crystals in water, the immersed portion will at once be coated with a bright deposit of metallic copper.

Mercury in Corrosive Sublimate.—Similarly this white crystalline substance called corrosive sublimate, a very poisonous body, contains the metal mercury. If we dissolve a little of it in water and dip a bright strip of copper, or a bright halfpenny, in the solution, the red metal becomes coated with a gray deposit of metallic mercury, which, if we rub it with the finger, will show a shining silvery layer of quicksilver.

EXPT. 18. **Silver and Lead contained in white Crystalline Salts.**—Again, this white crystalline solid substance, called lunar-caustic, contains silver. If some of it be dissolved in a little distilled water in a test-tube, and a little grape sugar and caustic soda be added and the mixture warmed, we get the inside of the test-tube *silvered* by a thin coating of beautifully bright metallic silver. And again this other white compound (sugar of lead). If we dissolve a small quantity of it in water and hang a small piece of zinc in the solution in a tumbler, it will yield, after a few hours, a beautiful tree-like growth of metallic lead called the lead tree. In these experiments a chemical reaction has taken place; the iron has taken the place of the copper in the copper compound, and formed a new compound of iron, whilst metallic copper is liberated or set free in the pure state. Similarly, copper has replaced the mercury, and zinc the lead, new compounds of copper and zinc being formed, whilst the mercury and lead are set free in the metallic state.

Symbols.—It is not always convenient to use the full names of the elements when we write them down, so chemists have devised *Symbols* which are to stand for them. These symbols are generally the first letter of the name or sometimes the first two letters; and often where the first letter has once been used, a second element, whose name begins with the same letter, is denoted by the first letter or the first two letters of the Latin or Greek names.

The following will serve as examples:

NAMES.	SYMBOLS.	NAMES.	SYMBOLS.
Carbon	C	Sulphur	S
Calcium	Ca	Sodium	Na (Natrium)
Cobalt	Co	Silicon	Si
Copper	Cu (Cuprum)	Silver	Ag (Argentum)
Iodine	I	Nitrogen	N
Iron	Fe (Ferrum)	Nickel	Ni
Phosphorus	P	Magnesium	Mg
Potassium	K (Kalium)	Mercury	Hg (Hydrargyrum)
Platinum	Pt	Hydrogen	H
Lead	Pb (Plumbum)	Oxygen	O

These symbols mean a very great deal more than the mere names of the elements, as we shall see as we get farther on.

They are also used to denote compounds by placing the symbols close together. When two symbols are placed close together it means that the two elements denoted by them are *chemically combined* and form a compound, *e.g.*:

HgO	means	Oxide of	Mercury
CuO	„	„	Copper
CaO	„	„	Calcium (or Lime)
MgO	„	„	Magnesium

and so on.

Formulæ and Equations.—These double symbols are called formulæ (singular, formula), and it is by means of these formulæ that the chemist expresses all his chemical reactions in *equations*. The following will serve as examples of equations:—



(Combination) $Hg + O = HgO$,

meaning that mercury and oxygen have combined, as in Lavoisier's experiment, to form the red powder, oxide of mercury.



(Combination) $Cu + O = CuO$

denotes the formation of oxide of copper from metallic copper and oxygen, *e.g.* when Cu is very strongly heated in air, it becomes covered with black scales of oxide of copper.



(Decomposition) $HgO = Hg + O$.

This denotes that the red powder has been again decomposed into its elements. It will be noticed that on the left-hand side is placed the condition of the elements or compounds before the chemical reaction (whether combination or decomposition) has taken place, whilst on the right-hand side are placed the products or ultimate result of the chemical action, and this order is invariably followed, thus:—



(Combination) $Hg + O = HgO$.



(Decomposition) $HgO = Hg + O$.

Matter is indestructible, it can neither be created nor destroyed. It can only change its form by entering into new

combinations; therefore, there is *always the same weight of materials on each side of an equation*—*e.g.* in the above equations the weight of mercury and the weight of oxygen added together are exactly equal to the weight of the oxide of mercury.

What we have learnt

In our fourth Lesson we have learnt that all substances may be classified as elements and compounds. Elements are substances which have not been chemically decomposed into two or more different bodies. Compounds are substances formed by the union or combination of two or more elements. We have seen that compounds differ in the most marked manner from the elements of which they are composed. The elements are divided into metals and non-metals. Symbols are used to denote the names of the elements, whilst formulæ are used to denote the composition of *compounds*. Equations are used to exhibit chemical reactions by means of symbols and formulæ.

Exercises on Lesson IV

1. Give five examples each, of elements and compounds.
2. Give four gaseous and four solid non-metals.
3. What is a compound?
4. Write out three formulæ and three equations.
5. How can you show that blue vitriol contains copper, and that corrosive sublimate contains mercury?
6. What is the difference in meaning between the equation $HgO = Hg + O$ and that $Hg + O = HgO$?
7. What elements are denoted by the following symbols, Fe, I, Ni, Mg, Hg, Ag, Na, S, Si, K, Pt, Pb, Co, Cu?
8. What are the symbols for mercury, lead, sulphur, silver, silicon, sodium, iron, iodine?

LESSON V

COMBINATION IN DEFINITE AND MULTIPLE PROPORTIONS — DALTON'S ATOMIC THEORY — ATOMIC AND MOLECULAR WEIGHTS—CALCULATIONS.

Constancy of Chemical Composition.—These symbols, formulæ, and equations have a far wider meaning than is indicated in the preceding lesson; and to understand what that meaning is, we must try to master the laws of combination in definite and multiple proportions.

To understand this most important subject let us begin with a simple illustration. By long experience and many experiments, chemists have found that every chemical compound has a fixed and definite composition. No matter how it is made or where obtained, any given chemical compound, whether found in nature or artificially made, if carefully *analysed* is always found to contain exactly the same proportion by weight of the elements of which it is composed.* Thus for example, if we take 215 parts of the red powder, oxide of mercury, and then decompose it by heat, and are careful not to allow any of the mercury to escape as vapour, we obtain 199 parts of liquid metallic mercury, whilst 16 parts by weight of gaseous oxygen escape. Similarly, if we take 24 parts by weight of the metal magnesium and burn it carefully so as not to lose any of the white fumes, we get 40 parts by weight of oxide of magnesium, and we must remember that in burning, magnesium is combining with oxygen. Again, if we take 79 parts by weight of black oxide of copper and abstract all its oxygen from it (as we can do by heating it strongly in a current of hydrogen gas, the hydrogen combining with the oxygen to form water which escapes as steam, leaving metallic copper behind), we find that 63 parts of metallic copper remain, and 16 parts of oxygen have disappeared. Therefore, these oxides have the following composition by weight:—

* Chemical compounds are thus sharply distinguished from mechanical mixtures which may be made up in any wished for proportion and between the constituents of which there is no *chemical union* or *combination*. See Expt. 13, p. 16.

Mercury 199*	Magnesium 24*	Copper 63*
Oxygen 16	Oxygen 16	Oxygen 16
Oxide of Mercury 215	Oxide of Magnesium 40	Oxide of Copper 79

Relations between the Combining Weights.—If now we compare the *sulphides* of these metals (the sulphides are compounds formed by the combination of the metals with sulphur, just as oxides are the compounds formed with oxygen) we find the following are the proportions:—

Mercury 199	Magnesium 24	Copper 63
Sulphur 32	Sulphur 32	Sulphur 32
Sulphide of Mercury 231	Sulphide of Magnesium 56	Sulphide of Copper 95

Similarly with the chlorides—combinations of the metals with chlorine—we have the following numbers:—

Mercury 199	Magnesium 24	Copper 63
Chlorine 70	Chlorine 70	Chlorine 70
Chloride of Mercury 269	Chloride of Magnesium 94	Chloride of Copper 133

Here we see a remarkable relation existing between the given weights of the three metals and a constant weight of another element, this constant being a different one for each element taken. Thus if we always take the same proportions of the metals, namely, 199 parts of mercury, 24 parts of magnesium, and 63 parts of copper, we find that a constant weight of some other element, 16 of oxygen, 32 of sulphur, or 70 of chlorine, will be required to combine with the metals to form a definite compound.

This remarkable relation was, however, not at once seen by chemists; they were accustomed to express their chemical compositions by giving the number of parts of each element required to make up 100, as in the figures below, and in the

* It is evident that these weights of the three metals are *equivalent* to each other in combining power, because they combine severally with identical quantities of the other elements, oxygen, sulphur, and chlorine. The *equivalent* of an element may be defined as that weight of it which will combine directly with, or displace from one of its compounds, *one part by weight of Hydrogen* (or its equivalent). See Equivalents and Atomic weights, p. 241, Appendix.

numbers expressing percentage composition no definite relation seemed to exist.

Up to the time of John Dalton (1808), there was no satisfactory manner of accounting for this remarkable constancy of the exact proportions in which the elements were found combined together in compounds. *Apparent exceptions* to the uniform constancy of composition, however, led John Dalton to formulate a theory which accounted in a completely satisfactory manner for all the ascertained facts, the importance of which theory cannot be over-estimated, for it forms one of the principal foundation-stones of the exact science of chemistry. Dalton was acquainted with several cases in which two elements combined together in two *different* proportions, *e.g.* carbon and oxygen, and carbon and hydrogen each formed two compounds thus :—

	(1)	(2)
Carbon	42.86	27.27
Oxygen	57.14	72.73
	100.00	100.00

	(1)	(2)
Carbon	85.68	74.95
Hydrogen	14.32	25.05
	100.00	100.00

These figures show no definite relation one to the other, but Dalton asked himself what was the relation of one element, say oxygen, in both compounds when the other element (carbon) remains constant? In other words, how much oxygen in each case combines with the unit weight of carbon? Let us calculate this. Divide 42.86 and 57.14 by 42.86; we get 1 of carbon and 1.33 of oxygen. Then divide 27.27 and 72.73 by 27.27; we get 1 of carbon and 2.66 of oxygen, or

1st Compound.	2nd Compound.
Carbon = 1	Carbon = 1
Oxygen = 1.33	Oxygen = 2.66

Now we see a definite relation between the two quantities of oxygen, for we find that for the same weight of carbon, the oxygen in the second compound is *exactly double* that in the first. In the same way the hydrogen compounds contain

1st Compound.	2nd Compound.
Carbon = 1	Carbon = 1
Hydrogen = 0.167	Hydrogen = 0.334 ;

or in the second compound, for the same weight of carbon, the amount of hydrogen is *exactly double* the amount in the first compound.

Again a series of five compounds of nitrogen and oxygen are now known (which we shall study more fully afterwards). Looking at their percentage chemical composition, no particular relation or ratio between the figures is noticed.

	(1)	(2)	(3)	(4)	(5)
Nitrogen	63.6	46.6	36.8	30.4	25.9
Oxygen	36.4	53.4	63.2	69.6	74.1
	100.0	100.0	100.0	100.0	100.0

If, however, we calculate the weight of oxygen combined with a constant weight of nitrogen (say 27.8 parts of nitrogen*), we find, as in the foregoing examples, that oxygen is present in the simple ratios 1 : 2 : 3 : 4 : 5, thus:—

	(1)	(2)	(3)	(4)	(5)
Nitrogen	27.8	27.8	27.8	27.8	27.8 *
Oxygen	15.9	31.8	47.7	63.6	79.5

There are a very great many examples of two elements forming several compounds in this manner; but taking a constant weight of one element, the other is always present in weights which are either simple multiples of the lowest weight, or which have a very simple relation one to the other, such as

1 : 2   2 : 3   3 : 5

These facts are expressed in Dalton's *Laws of combination in Definite and Multiple proportions.*

Dalton's Atomic Theory. — These facts are explained by the following *theory*, known as Dalton's Atomic Theory, which is of such importance that the student must understand it thoroughly. He assumed, following the views of the old Greek philosophers, that all matter is made up of exceedingly small invisible particles called atoms (from *α* privative, and τέμνω I cut), that these atoms cannot be divided into two smaller portions; in other words, that the atom is the smallest particle of matter

* 27.8 is twice the atomic weight of nitrogen (see p. 33).

which can exist. He further assumed that chemical combination consists in the joining together of the atoms of the combining elements to form a *group of atoms* or a *molecule* * which are bound to each other by their mutual chemical attraction. Further, that all the atoms of the same element are of exactly the same weight, and possess the same properties, and that atoms of different elements are different in weight, and possess other properties.

We can now see why chemical compounds possess a constant composition, because each molecule of a compound is exactly like every other molecule—it is composed of the same number of atoms of the same kinds and possessing the same weights. Hence the whole mass of a substance consisting of millions of molecules will contain just the same proportion of the component elements as a single molecule does. Further, suppose we have a molecule, say of one atom of carbon and one atom of oxygen. To make a compound containing more oxygen, we must add at least one more atom, we cannot add part of an atom, but the addition of another atom of oxygen to every molecule exactly doubles the proportion of oxygen, the carbon remaining constant, and this is in accordance with the facts. Similarly with the five compounds of nitrogen and oxygen. The first compound only contains one atom of oxygen, the second two, the third three, and so on; the fifth compound contains five atoms of oxygen in the molecule. We cannot have any intermediate compounds according to Dalton's atomic theory, and this harmonises with the facts, for it has hitherto been found impossible to prepare any intermediate compounds of nitrogen and oxygen.

Evidently then it is possible to find out by chemical analysis, not only the percentage composition of a body, but also the relative weights of the atoms. This has been done for all the elements at present known, and as hydrogen is the lightest substance known, *the atom of hydrogen is taken as the unit of weight.* Therefore we say that the atomic weight or the weight

* Sir William Thomson (now Lord Kelvin) has calculated that if a drop of water could be magnified so as to appear as large as the earth, the molecules would appear about as large as cricket balls. How many millions of millions of molecules then must there be in a drop of water!

of the atom of hydrogen is 1 or H = 1. We have seen that sodium displaces hydrogen from water;



$$H_2O + Na = NaOH + H.$$

If we find out how many grams of sodium are required to displace one gram of hydrogen, we obtain the atomic weight of sodium. This is found to be 22.9.* Caustic soda, the first product of the action of sodium on water, is found still to contain as much hydrogen as the water has lost. Therefore the molecule of water must contain two atoms of hydrogen. This is confirmed by the fact that in the electrolysis of water we get twice as large a volume of hydrogen as of oxygen. Therefore we write the formula of water H_2O; the little 2 is placed beneath and to the right of the symbol to denote two atoms.

Water is found to be composed of 2 parts by weight of hydrogen and 15.9 parts by weight of oxygen, so we say the atomic weight of oxygen is 15.9, and oxygen gas is found to be exactly 15.9 times as heavy as hydrogen gas.

By similar methods the *atomic weights* of all the known elements have been found. But all the minute precautions and all the abstruse considerations which are taken into account in finding them cannot be entered into here. Suffice it to say that, as the atomic weights of the elements are of the utmost importance and will be constantly needed in subsequent lessons, it will be well here to give a list of them. Only those elements which are most important, or which are most plentiful and useful to man, are given.

The names printed in large capital italics are the non-metals; those in small Roman capitals are the metals. For an explanation of the differences between metals and non-metals see p. 245, Appendix.

List of Elements and their Atomic Weights.—

NAMES.	SYMBOLS.	ATOMIC WEIGHTS.†
ALUMINIUM	Al	26.9
ANTIMONY	Sb (Stibium)	119.4
ARSENIC	As	74.4
BARIUM	Ba	136.0
BISMUTH	Bi	206.4

* This number is also *the equivalent* of sodium, because that weight of sodium is capable of displacing *one part by weight of hydrogen* from one of its compounds. See Equivalents and Atomic Weights, p. 241, Appendix.

† The above atomic weights are given to one place of decimals only, as being sufficiently accurate for use in elementary work.

NAMES.	SYMBOLS.	ATOMIC WEIGHTS.
BORON	B	10.7
BROMINE	Br	79.4
CADMIUM	Cd	111.3
CALCIUM	Ca	39.7
CARBON	C	11.9
CHLORINE	Cl	35.2
CHROMIUM	Cr	51.9
COBALT	Co	58.6
COPPER	Cu	62.8
FLUORINE	F	18.9
GOLD	Au (Aurum)	195.7
HYDROGEN	H	1.0
IODINE	I	125.9
IRON	Fe (Ferrum).	55.6
LEAD	Pb (Plumbum)	205.4
MAGNESIUM	Mg	24.2
MANGANESE	Mn	54.6
MERCURY	Hg (Hydrargyrum)	198.9
NICKEL	Ni	58.6
NITROGEN	N	13.9
OXYGEN	O	15.9
PHOSPHORUS	P	30.8
PLATINUM	Pt	193.3
POTASSIUM	K (Kalium)	38.9
SILVER	Ag (Argentum)	107.1
SILICON	Si	28.2
SODIUM	Na (Natrium)	22.9
SULPHUR	S	31.8
TIN	Sn (Stannum)	117.2
ZINC	Zn	65.0

There are other elements (making in all about 70), which are rare or not of such importance as those named.

We are now in a position to understand how necessary it is to know the atomic weights of the elements, and also the exact composition of any chemical compound. We now see that a chemical formula not only expresses the nature of the elements composing the compound, but also gives its quantitative composition or the proportions by weight in which each element is present. In many cases chemical compounds contain two, three, or more atoms of the same element, and when this is the case we must modify the simple formulæ which we have previously used by adding a small figure just beneath and to the right of the symbol of such element.

The *symbol* of an element represents *one atom* and the formula of a compound represents *one molecule.*

In the five compounds of nitrogen and oxygen, for example, we see on looking at the table of atomic weights that N = 13.9 and O = 15.9; but the first compound contains N 27.8 and O 15.9, therefore there are two atoms of nitrogen and one atom of oxygen in the molecule, and the formulæ of the five compounds may be expressed as N_2O, N_2O_2,* N_2O_3, N_2O_4,* and N_2O_5.

The carbon and oxygen compounds are CO and CO_2.
The carbon and hydrogen „ „ CH_2† „ CH_4.

Calculations.—Let us now take a few examples of the way in which these atomic weights are used in calculations of weights of materials used in chemical reactions. Potassium chlorate is a white solid body having the formula $KClO_3$. This, when strongly heated, decomposes, and gives off all its oxygen, leaving behind a compound called potassium chloride (KCl).

Example.—Find out how many ounces of potassium chloride remain, on completely decomposing 100 ounces of $KClO_3$, and also calculate the percentage composition of the latter compound.

Directions.—1. If a chemical action occurs, always write out the equation expressing it.

2. Write down the symbols of the various elements of the compounds concerned in the calculation under each other, and place the atomic weights on their right, not forgetting to multiply the atomic weights by the number of atoms where more than one atom of any element is present as in $KClO_3$, Oxygen = 15.9 × 3. Next add up the numbers to obtain the molecular weight, or weight of a single molecule. In the third term of the proportion sum that follows place the given weight of substance. In the first term place the atomic or molecular weight of the substance occurring in the third term. In the second term place the atomic or molecular weight of the substance sought.

$$KClO_3 = KCl + 3O.$$

$$\left.\begin{array}{l} K = 38.9 \\ Cl = 35.2 \end{array}\right\} 74.1 = KCl.$$

$$O_3 = 47.7 \quad 47.7 = 3O.$$

$$\underline{121.8} \quad \underline{121.8} = KClO_3$$

* We shall see later that these formulæ should be NO and NO_2, but the ratio between the nitrogen and oxygen is not thereby altered, so the argument is unaffected.

† Similarly, the formula of this compound is really C_2H_4 (see p. 232), but the ratio between the carbon and hydrogen is not altered.

Therefore 121.8 parts (grams, ounces, lbs., or tons) of $KClO_3$ yield 47.7 parts of oxygen, and 74.1 parts of KCl. Then, by simple proportion as above described, we have

$$121.8 : 74.1 :: 100 : \text{Ans.}$$

$$= \frac{74.1 \times 100}{121.8} = \frac{7410}{121.8} = 60.84. \quad \text{Ans.}$$

Answer: 60.84 parts of potassium chloride remain.

Second Method.—It may perhaps be easier for the younger readers to work out the above calculations by the method of reduction to unity, instead of by proportion as explained above. Let us take the first calculation on p. 34. In the second method we simply ask—

If 121.8 parts of potassium chlorate yield 74.1 parts of potassium chloride, what will 1 part yield? Evidently we must divide 74.1 by 121.8, or $\frac{74.1}{121.8}$. Then, if 1 part yields $\frac{74.1}{121.8}$, what will 100 yield? Evidently $\frac{74.1}{121.8} \times 100$, or $\frac{74.1 \times 100}{121.8}$, or $\frac{7410}{121.8}$, which is exactly what we come to by the first method. Or

If 121.8 gives 74.1

$$1 \quad ,, \quad \frac{74.1}{121.8}$$

$$\therefore 100 \quad ,, \quad \frac{74.1}{121.8} \times 100$$

All the other calculations can be worked out in the same way.

If we calculate in the same way how many ounces of oxygen the compound has lost, the two answers should add up to 100. Let us see if they do.

$$121.8 : 47.7 :: 100 : \text{Ans.}$$

$$= \frac{47.7 \times 100}{121.8} = \frac{4770}{121.8} = 39.16. \quad \text{Ans.}$$

Answer: 39.16 parts of oxygen given off.

∴ Oxygen given off	39.16%
Potassium chloride left behind	60.84%
Potassium chlorate decomposed .	100.00

If we find the percentage of K, and subtract it from 60.84 to obtain the chlorine, we obtain the percentage composition of $KClO_3$. Thus

$$121.8 : 38.9 :: 100 : \text{Ans.}$$

$$\frac{38.9 \times 100}{121.8} = \frac{3890}{121.8} = 31.94\% \text{ of potassium.}$$

The percentage composition is therefore

K	31.94%	} KCl = 60.84%.
Cl	28.90%	
O_3	39.16%	
$KClO_3$	100.00	

Further Examples.*—(1) What weight of liquid mercury can be obtained by the decomposition of 4 ounces of oxide of mercury, HgO?



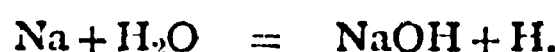
$$HgO = Hg + O.$$

Hg	199.0	
O	15.9	
HgO	214.9	

$$214.9 : 199 : : 4 : \text{Ans.}$$

$$= \frac{199 \times 4}{214.9} = \text{Ans.}$$

(2) From the following equation calculate what weight of sodium will be required completely to decompose 2 lbs. of water.

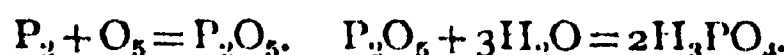


$$Na + H_2O = NaOH + H.$$

$$\left.\begin{array}{l} H_2(1 \times 2) = 2.0 \\ O \quad = 15.9 \end{array}\right\} H_2O = 17.9. \quad Na = 22.9.$$

$$17.9 : 22.9 : : 2 \quad = \quad \frac{22.9 \times 2}{17.9} = \text{Ans.}$$

(3) How much phosphoric acid, H_3PO_4, will be produced by burning 2 ounces of phosphorus in a closed bell jar over water?



$$P_2 + O_5 = P_2O_5. \quad P_2O_5 + 3H_2O = 2H_3PO_4.$$

Two atoms of phosphorus yield 2 molecules of phosphoric acid, therefore 1 atom of P yields 1 molecule of H_3PO_4.

$H_3(1 \times 3)$	= 3.0
P	= 30.8
$O_4(15.9 \times 4)$	= 63.6
H_3PO_4	= 97.4

$$30.8 : 97.4 : : 2$$

$$= \frac{97.4 \times 2}{30.8} = \text{Ans.}$$

(4) How many ounces of water will be required to form phosphoric acid, H_3PO_4, with 6 ounces of P_2O_5?



$$P_2O_5 + 3H_2O = 2H_3PO_4.$$

* The student should work out these calculations himself.

Therefore 3 molecules of water are required for each molecule of oxide of phosphorus, and we must not omit to multiply by 3.

$$3H_2O = (2 + 15.9) \times 3 = 53.7$$

$$\begin{array}{lll} P_2 & (30.8 \times 2) = & 61.6 \\ O_5 & (15.9 \times 5) = & 79.5 \\ P_2O_5 & & = 141.1 \end{array} \qquad 141.1 : 53.7 :: 6 \quad = \frac{53.7 \times 6}{141.1} = \text{Ans.}$$

Calculation of Formulæ.—As the converse of the first example given on p. 34, if we know the percentage composition of a compound it is easy to calculate its simplest formula. For if we divide the percentage of each element by its atomic weight and divide each number so obtained by the lowest, we obtain the ratio between the number of the atoms, *e.g.*—

K = 38.9	31.94% K	$\frac{31.94}{38.9} = 0.821$	$\frac{.821}{.821} = 1 = K.$
Cl = 35.2	28.90% Cl	$\frac{28.90}{35.2} = 0.821$	$\frac{.821}{.821} = 1 = Cl.$
O = 15.9	39.16% O	$\frac{39.16}{15.9} = 2.463$	$\frac{2.463}{.821} = 3 = O_3.$

Therefore the formula of potassium chlorate is $KClO_3$.

WHAT WE HAVE LEARNT

In the fifth Lesson we have learnt a wider meaning of symbols, formulæ, and equations. Constancy of composition of all compounds. Combining weights and the relations between them. Combination in multiple proportions, illustrated by oxides and hydrides of carbon, and the five oxides of nitrogen. Explanation of above facts by Dalton's Atomic Theory. Meaning of atomic weights, of which a list is given. Method of using atomic weights in the calculation of percentage compositions, and the weights of materials taking part in chemical reactions.

EXERCISES ON LESSON V

1. What is meant by the constancy of composition of chemical compounds?

2. A chemical compound is found to consist of hydrogen 3.08%, phosphorus 31.62%, oxygen 65.30%. What is its simplest formula?

3. Give some examples of chemical combination in multiple proportions; why were not the relations between the combining weights at once seen?

4. Give an account of Dalton's Atomic Theory.

5. Work out the numerical examples given in the lesson.

6. Calculate the percentage composition of manganese dioxide, MnO_2, potassium nitrate, KNO_3, and sodium sulphate, Na_2SO_4.

7. How much sodium shall I require in order to obtain 400 grams of pure caustic soda?

8. From the percentage compositions of the oxides of nitrogen given on p. 30, calculate their *simplest* formulæ.

LESSON VI

PHYSICAL MEASUREMENTS

STANDARDS OF LENGTH, VOLUME, AND WEIGHT USED IN CHEMICAL EXPERIMENTS—METHODS OF WEIGHING AND MEASURING—THE METRIC SYSTEM—THE THERMOMETER—MEASUREMENTS OF TEMPERATURES—CONVERSION OF THERMOMETRIC SCALES.

Standards of Length.—The standard unit of length in the metric system, which is now generally used for scientific purposes, is the metre (m.). This is divided into tenths (decimetres), and into hundredths (centimetres) and

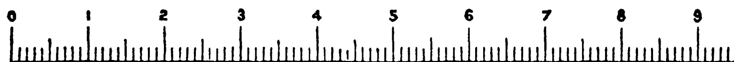


Fig. 12

thousandths (millimetres). Fig. 12 is an exact copy of a decimetre scale, divided into 10 centimetres and into 100 millimetres. The scale is, therefore, one-tenth of a metre in length (decimetre).

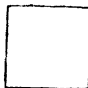
Thus we have

1 decimetre (dcm.) = 0.1 m.	10 dcm. = 1 m.	10 m. = 1 deca-m.
1 centimetre (cm.) = 0.01 ,,	100 cm. = 1 ,,	100 m. = 1 hecto-m.
1 millimetre (mm.) = 0.001 ,,	1000 mm. = 1 ,,	1000 m. = 1 kilo-m.

For the relation between the English and metric systems, see Appendix.

The Measures of Area are easily obtained from the

standards of length. Thus square metre, square decimetre, square centimetre, square millimetre. Fig. 13 is exactly a square centimetre, a cube on this base would be a cubic centimetre, the unit of volume, which, as we shall see presently, is closely related to the *gram*, the unit of weight.


Fig. 13.

The Standards of Volume.—The unit of volume is the cubic centimetre, but one cubic decimetre = 1000 cubic centimetres is the common unit of volume, and is called a *litre*, and we have decalitre = 10 litres, hectalitre = 100 litres, kilolitre = 1000 litres.

1 cubic centimetre	= unit	10	litres	=	deca litre.
100 cc.	= decilitre	100	,,	= hecta	,,
1000 cc.	= litre	1000	,,	= kilo	,,

The Standards of Weight.—The standard of weight is the weight of a cubic centimetre of distilled water at its point of maximum density, 4° C.,* weighed at Paris,† and this weight is called a gramme, or (English) *gram*. The common unit is a kilogram, or 1000 grams.

1 gram =	10 decigrams	10 gr.	= 1 deca-gr.
=	100 centigrams	100 ,,	= 1 hecto-gr.
=	1000 milligrams	1000 ,,	= 1 kilo-gr.

The Chemical Balance.‡—In all important chemical

* The reason for taking 4° is explained on p. 102.

† The true weight of a body varies at different places on the earth's surface, because the attraction of gravitation is not uniform. Owing to the earth being flattened at the poles and bulged out at the equator, and also owing to its rotation, a substance (say a gram weight) weighed on a spring balance at the poles will be nearer the centre of the earth (at which point the attractive force of gravitation may be supposed to act) and will weigh more than if weighed at the equator. Hence, to be strictly accurate in such an important matter as defining the standard of weight, it is necessary to state the place at which the standard is correct. *e.g.* A gram weight will weigh exactly a gram at Paris, but more than a gram at London, and still more at the poles. But although its weight varies, its *mass*, or the quantity of matter it contains, will be the same everywhere—and if it is desired to eliminate the varying force of gravity, we speak of the mass of a body instead of its weight. Its *mass* is constant, but its *weight* depends upon where it is weighed, because the attractive force which gives bodies weight, viz. gravitation, varies at different places.

‡ For further information about the balance and methods of weighing consult Stewart and Gee's *Practical Physics*, vol. i., from which book Figs. 14-16, 19-21, and 59 have been taken.

experiments which have for their object the determination of the quantitative chemical composition of substances, the chemist makes use of delicate instruments for measuring and weighing all the materials which he uses. Perhaps the most important is the chemical balance, which consists essentially of (1) *the beam b*, or arms of the balance, which may be of brass or steel made in some such pattern as is shown in Fig. 15, so as to be as light and yet as rigid as possible. At each end are two knife edges of *agate*, *k*, turned upwards, and in the centre

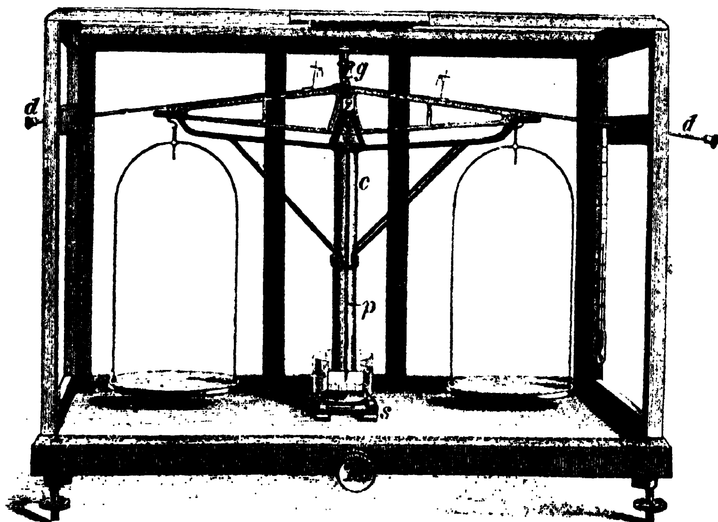


Fig. 14.

another knife edge, K, turned downwards. The centre knife-edge rests on a perfectly smooth plate of agate fixed on the pillar P of the balance. At the centre of the beam, and at right angles to it, pointing downwards, is a long pointer, *p*, which moves over a graduated scale. When the two sides are exactly balanced, the pointer rests at zero, the centre of the scale, whilst if either side be heavier than the other the pointer will move to the opposite side. There is a small vane *v* which may be moved to one side or the other, so as to adjust the

weight on each side very accurately, in order that when the pans are unloaded the pointer may vibrate equally on each side of the zero point. The two pans are suspended on the agate knife edges, which work with a minimum of friction

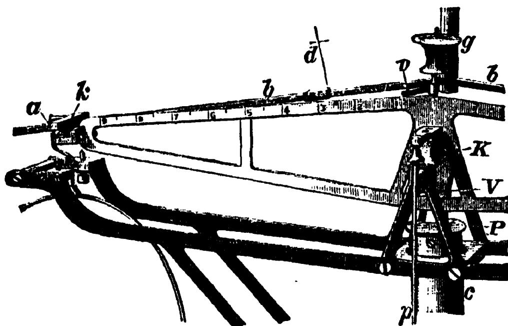
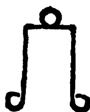


Fig. 15.

on agate planes. When not in use the pans may be lifted off the beam, and the beam from the pillar so as to support them on an independent arm, by a single turn of the large screw M. This preserves the knife edges from wearing, due to any vibration taking place when the balance is not in actual use.

Use of the Rider in exact weighing.—The beam is divided on each side into tenths and twentieths of its length measured between the two knife edges, and a very small weight called a *rider* (Fig. 16), because it is placed striding across the beam, may be moved along by means of the rod *d*, to any of the positions marked on the beam. This rider generally weighs a centigram, but if placed at $\frac{1}{10}$ the arm-length from the centre its effect is just $\frac{1}{10}$ of what it would be if placed on the pan, just as in the lever, Fig. 17, which would be in equilibrium with a 1 lb. weight at one end, and a 10 lb. weight at the other if the distances between the knife edges were as 10 to 1. The 10 lb. weight has the same effect at unit distance as a 1 lb. weight has at 10 times the distance from the central support. Evidently then if we place our rider at a position on the beam marked 7.3, and the balance is in equilibrium, it denotes a weight on the opposite pan of 7.3 tenths of a centigram, or .0073 gram. It would not be convenient to make weights so small as .0001 gram, or the ten-thousandth of a gram, yet by means of


Fig. 16.

the *rider* it is easy to detect accurately on a good balance a difference equal to this slight amount by means of a weight 100 times as heavy (and yet this is only a small piece of twisted aluminium wire).

When each pan contains a weight equal to 100 grams, a good balance will indicate a difference of a tenth of a milligram, or .0001 gr., therefore it will indicate a difference of a $\frac{1}{1000000}$, a millionth part of the load. For making delicate weighings the balance must be enclosed in a glass case, so as to protect it from air currents, which would have the effect of disturbing the equilibrium. To protect the balance from the effects of moisture and rust, especially if it has steel arms, it is usual to place inside the balance case a funnel containing dry calcium chloride, which rests in an empty bottle and which will absorb the moisture readily, and preserve a dry interior.

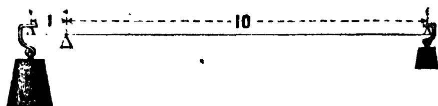


Fig. 17.

Conditions of Sensitiveness and Equilibrium.—The conditions which must be observed to make the balance *sensitive* are (1) the beam to be as light and as long as possible consistent with rigidity, and (2) the centre of gravity of the whole (beam, pans, and weight) to be below, and as near as possible to the centre of suspension.

The whole weight (of beam, pans, and weights) may be supposed to act at its centre of gravity E, the turning weight must raise this weight to *e* at a distance *Sa* from the point of support, so as to be in equilibrium. It is evident that if the centre of gravity of the whole be at E′, twice as far away from the axis of support, it will require twice as great a weight to give the same deflection of the balance, because the weight must then be moved twice as far away (*Sb*) from the point of support. The gravity-bob *g* at the centre of the beam is made to turn up and down, so as to adjust the point of the centre of gravity as near as possible to the centre

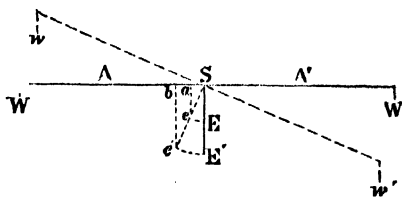


Fig. 18

of support. Then the whole weight acting at E must be moved an exceedingly small distance *Sa* from the point of support. If the centre of gravity E comes *above* the point S, the system is in a position of unstable equilibrium, and the beam would overturn with the least touch; whilst if S and E are coincident, the beam would be in equilibrium in any position (neutral equilibrium). The *accuracy* depends on the two arms being of exactly the same length, and this may be tested by weighing a substance first on one pan and then on the other—if both weighings agree, then the arms are equal. $W \times A = W' \times A'$, therefore if $W = W'$, then $A = A'$, and since W and W′ are equal, they may be interchanged, then $W' \times A = W \times A'$.

If the two weighings do not agree, the arms are unequal, and the true weight is found by taking the square root of the product of the two apparent weights.

Method of Weighing—the Weights.—The set of weights used for exact work in chemistry usually consists of 500, 200, 100, 100 grams; 50, 20, 10, 10 grams; 5, 2, 1, 1, 1 grams, making up a kilogram; then .5, .2, .1, .1, .05, .02, .01, .01, and a couple of riders, each equal to a centigram; sometimes .005, .002, .001, .001 are present in the set, but are seldom used, the rider doing all that is necessary below 0.01. The substance to be weighed is placed in the left pan, and the nearest weight is placed on the right; if this is too heavy, the next lower is taken, and so on until it is balanced to a centigram; the final adjustment is made by means of the rider, which is moved along the arm until the pointer vibrates equally on both sides of the zero point. Suppose the weights are 50, 2, 1, .2, .05, and the rider at 7.3, the weight of the substance is 53.2573 grams.

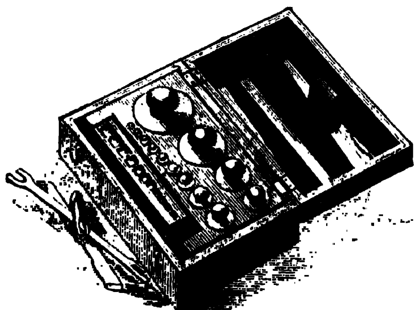


Fig. 19

How to measure Volumes of Liquids exactly.—For this purpose marked measuring flasks are used (Fig. 20); these have a circular mark *c* etched on the neck, and must be filled exactly to this mark, at a standard temperature. For withdrawing a definite volume of a liquid, pipettes are used

(Fig. 20); the point of the pipette is immersed in the liquid, which is sucked up by the mouth as far as possible. The finger is then quickly placed on the top of the pipette, and carefully released just a little to allow air to enter; this enables the liquid to flow out until the mark *a* on the stem is reached, when the desired volume is obtained. When intermediate volumes are required, graduated cylinders, pipettes, or burettes (Fig. 21) are employed.



Fig. 20.


Fig. 21.

Measurement of Temperature, the Thermometer.—As all bodies—solid, liquid, and gaseous—expand when heated, it is necessary to be able to ascertain their temperature, so that their volume at a constant temperature may be known.

EXPT. 19.—Here is a large glass bulb filled with a coloured liquid to a mark on the stem at the ordinary temperature of the air. On plunging this into a large beaker of hot water, we notice first an immediate but slight *fall* in the level of the liquid, and directly afterwards the liquid begins to rise again, and, passing the first point, rises high in the stem. Fig. 22 shows that the first effect of the heat was to expand the solid glass bulb and make it larger, and hence the fall, for to fill it to the same mark more liquid is required. The heat, however, soon reaches the liquid, and it too begins to expand; *but it expands much more* than the solid glass, hence it not only fills the enlarged bulb to the same place from which it started, but it rises higher and higher, to the second mark on the stem.

EXPT. 20.—Similarly, that gases expand by heat may be shown by fitting up a large flask with a delivery tube dipping into a pneumatic trough. By applying a Bunsen burner to the

outside of the flask, the contained air expands so much that a quantity of it escapes and ascends into the gas cylinder. On taking away the lamp, however, the air soon cools down again, and in cooling *contracts*, and the water rises up the delivery tube into the neck of the flask to take the place of the air which has escaped (Fig. 23).

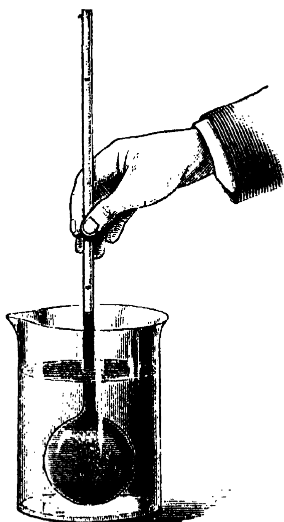


Fig. 22.

Hence it is quite evident that if we want to know accurately the volume of any solid, liquid, or gas, we must know their temperature, for they occupy different volumes at different temperatures.

The thermometer is used for measuring temperature. It consists of a thick glass tube with an extremely fine bore, terminating in a spherical or cylindrical bulb, containing a liquid, generally mercury or alcohol. Mercury is most often used, because it expands uniformly, and because it solidifies at an extremely low temperature and boils at a very high temperature; in other words, a mercurial thermometer has a very great range. The thermometer is made in the following manner. The open end is enlarged into a little cup, which is filled with mercury; the bulb is heated by a Bunsen flame; this expels a portion of the air, and on cooling, a portion of mercury enters the bulb (Fig. 24). By alternate heating and cooling, *all* the air is expelled, and the bulb and stem completely filled with mercury. It is then heated to the boiling point of mercury, and when it has cooled to the highest temperature which it is desired to measure, the end is sealed up by fusing the glass in a blowpipe. When the mercury cools it recedes in the tube and no air can enter.

Graduation of the Thermometer.—The next thing is to *graduate* the thermometer, and for this purpose two points are taken as starting-points from which to graduate

the whole stem. The first is obtained by plunging the

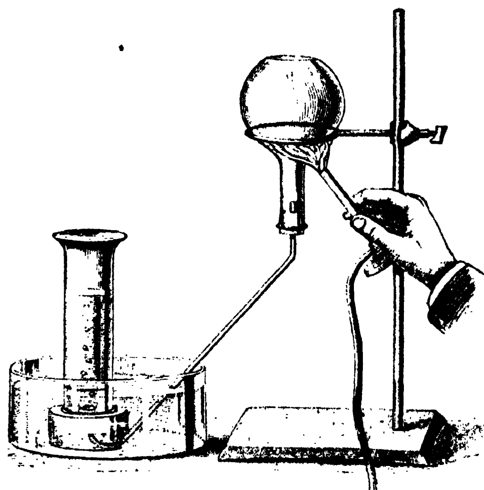


Fig. 23.

thermometer into melting ice, for ice melts at a constant temperature. When the position of the mercury becomes stationary, the height of the mercury in the stem is marked. The arrangement for marking the freezing point is shown in Fig. 25. The funnel is filled with broken ice in which the thermometer is inserted. Next the whole is placed in the steam escaping from boiling water in a jacketed tin boiler shown in Fig. 26; and this is also a constant or uniform temperature, if the experiment is always made at the same barometric pressure. When the height of the mercury has again be-

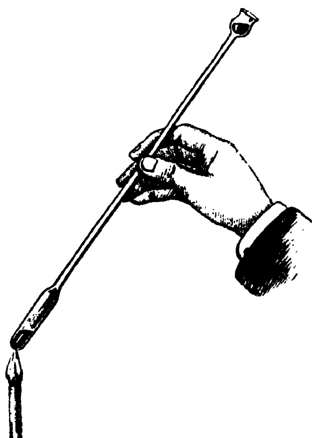


Fig. 24

come constant, this point is marked on the stem. We now have the positions of the freezing and boiling points of water (see p. 107 for influence of pressure).

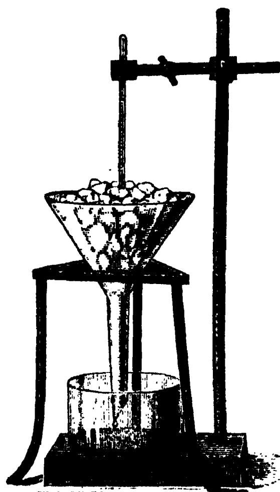


Fig. 25.

Centigrade, Fahrenheit, and Réaumur Scales.—The interval between the two points is divided differently in different countries, as shown in Fig. 27. In the Centigrade (or Celsius) thermometer the two points are marked 0 and 100, and the interval divided into 100 spaces. This scale is the one used in this book and in nearly all scientific experiments. On the Fahrenheit thermometer, which is commonly used in this country, the two points are marked 32 and 212 respectively (the zero point being supposed by Fahrenheit to be the greatest attainable cold), and the interval divided into 180 spaces, each being called one degree (1°). In the Réaumur the points are marked 0 and 80, and 80 spaces or degrees are made between them: this is used on the Continent. It is easy to convert any temperature from one scale to another. If we divide the whole interval in each by 20, we get equal intervals of temperature which contain

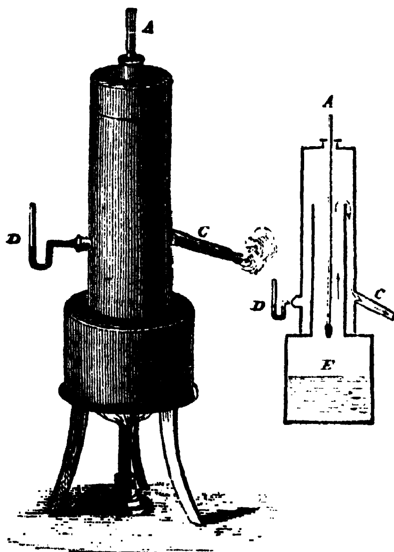


Fig. 26.

in C. 5, in F. 9, and in R. 4 spaces or degrees, so 5° C. = 9° F. = 4° R. So by proportion we can convert

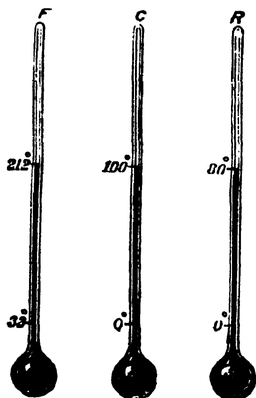


Fig. 27.

14° C. into R. $5 : 4 :: 14$

$$= \frac{4 \times 14}{5} = \frac{56}{5} = 11\tfrac{1}{5}° \text{ C.}$$

18° R. into C. $4 : 5 :: 18$

$$= \frac{5 \times 18}{4} = \frac{90}{4} = 22\tfrac{1}{2}° \text{ C.}$$

In converting from or into F. scale it is rather different. We must always take *the number of degrees above freezing point* in F. scale before beginning the conversion from F. to C., and we must *add* 32 to the answer if from C. to F., *e.g.*—

$$10° \text{ C. into F.} \quad 5 : 9 :: 10 = \frac{9 \times 10}{5} = 18. \quad 18 + 32 = 50° \text{ F.}$$

This is because the zero of F. is 32° below freezing point, and we always count from zero (or 0°); hence add 32.

To convert 60° F. into C. we have only 60 − 32 = 28° above freezing point, therefore

$$9 : 5 :: 28 = \frac{28 \times 5}{9} = \frac{140}{9} = 15\tfrac{5}{9}° \text{ C.}$$

What we have learnt

In our sixth Lesson we have considered the standards of length, area, volume, and weight in the metric system, which is now almost universally used for scientific purposes. We have learnt the methods adopted in weighing and measuring the volumes of substances by means of the balance and graduated glass vessels, such as the flask, pipette, and burette. Also the conditions of sensitiveness and equilibrium of the balance, and the use of the rider in exact weighing. We have learnt something about the expansion by heat, of solid, liquid, and gaseous bodies, together with the method of making and graduating a thermometer, and also the method of converting thermometric readings from one scale to another.

Exercises on Lesson VI

1. Explain the relations between the standards of length, area, volume, and weight in the metric system. How many millimetres are there in 4.739 metres, and how many centimetres in 3645 millimetres?

2. Describe the chemical balance and mention the conditions which must be observed to render it sensitive, giving reasons for your answer. How would you find out whether the arms of a balance are equal in length, and if unequal, how would you find the true weight of a substance by its means?

3. Describe an experiment to show that glass expands less than water for the same increase of temperature.

4. How are thermometers filled and graduated, and what are the different thermometric scales in use in different countries?

5. Convert 4° C. into F.; 5° F. into C. and R.; 60° F. into C. and R.; 18° R. into C. and F.; −40° F. into C.

6. Explain how the rider is used in exact weighing. What is the principle upon which it depends?

7. What relation exists between the position of the centre of gravity of a balance and its sensibility?

8. How is the centre of gravity of a balance adjusted?

9. Describe an experiment to show that gases expand when heated and contract when cooled.

LESSON VII*

PHYSICAL PROPERTIES OF GASES

RELATION OF VOLUME TO TEMPERATURE AND PRESSURE —DALTON'S LAW—BOYLE'S LAW—CALCULATION OF VOLUMES FROM WEIGHTS—REDUCTION TO NORMAL TEMPERATURE AND PRESSURE [NTP].

Relation of the Volume of Gases to Temperature. —We have seen in Expt. 20 that gases expand when heated and contract when cooled, and also in Expt. 19 that for an equal increase of temperature, solid bodies expand less than liquids, and these much less than gases; they also expand differently, whilst all gases are found to expand alike or very nearly so.

Law of Dalton.† —Dalton found that when the pressure is constant *all gases expand very nearly* $\frac{1}{273}$ *part of their volume at* 0° *for every increase in temperature of* 1° *C.* Thus

273 vols. of a gas at 0° C. become		
274	,,	1°
275	,,	2°
276	,,	3
273 + t	,,	t

Remembering this we can convert the volume of any gas

* In some cases it may be well to postpone this and the following lesson until after some of the subsequent lessons have been studied.

† This is also sometimes called the Law of Gay-Lussac and Charles, but it was first discovered by John Dalton.

measured at a particular temperature to the volume it would occupy at any other temperature, *e.g.* :—

Calculation of the Volumes of Gases at Different Temperatures.—A gas occupies 689 c.c. at 4° C., what vol. will it occupy at 15° C. ? 273 + 4 or 277 vols. at 4° C. become 273 + 15 or 288 vols. at 15°, and therefore

$$277 : 288 : : 689 = \frac{288 \times 689}{277} = \text{Ans.}$$

Directions.—Add 273 to each temperature. Then, as the third term of a proportion sum place the given volume, and in the second term place the higher number if the gas expands by heating from a lower to a higher temperature ; and the lower number if the gas contracts by cooling from a higher to a lower temperature, *e.g.*

Second Method.—These calculations also may be worked out by the method of reduction to unity explained on p. 35.

A gas occupies 1000 cc. at 20° C., what vol. will it occupy at 0° C. ?

$$273 + 20 = 293$$

$$293 : 273 : : 1000 = \frac{1000 \times 273}{293} = \text{Ans.}$$

EXPT. 21. **Relation of the Volume of Gases to Pressure.**—If we take a strong glass tube about 3 feet long, closed at one end, and fill it with liquid mercury, and then closing up the end tightly with the thumb, invert it in a basin full of mercury, we shall see, on removing the thumb, that the mercury falls in the tube and leaves a space in the upper part of about 6 inches long. If we incline this tube as shown in Fig. 28 to the second position B, in which the end of the tube falls below the level of the mercury in the first position A, we see that the mercury rises and completely fills the tube, showing that the space C of 6 inches did not contain any gas. This experiment was first made by

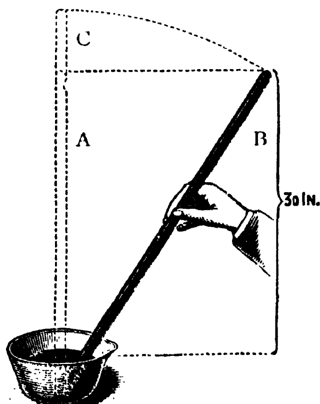


Fig. 28.

Torricelli, and the space C is called a Torricellian vacuum. Why does the mercury fall? and why does it rise in the tube when it is inclined? Why does not *all* the mercury run out? What keeps it up? These are the questions we may ask ourselves. The column of mercury is held up by the pressure of the atmosphere. The atmosphere rises to a height of at least 40 miles above the surface of the earth, and the accumulated weight of the mass presses on the mercury in the basin, and this in turn presses on the mercury in the tube, upholding a column of about 30 inches in height. When the tube is inclined as at B, the vertical height is less than 30 inches, so the mercury completely fills the tube. This column of mercury is the essential part of a mercurial *barometer* or pressure measurer. With atmospheric changes the pressure varies and the height of the column of mercury varies between wide limits, 2 or 3 inches frequently.

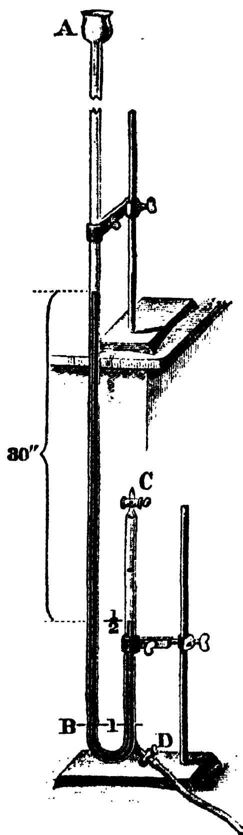


Fig. 29.

Let us now try some experiments to find out the relation between the volume of gases and the pressure to which they are subjected.

EXPT. 22. **Boyle's Law.**—Into the funnel A (Fig. 29) we will pour mercury until it is at level B in both tubes (the stopcock C being open). Closing C we enclose a unit volume of air at the ordinary pressure of the atmosphere, say the barometer is standing at 30 inches; let us now pour mercury into A until the difference in the levels in the U tube is 30 inches. Then in addition to the ordinary atmospheric pressure we have added a pressure of mercury equal to *another* atmosphere; so our air is under a pressure of two

atmospheres, and we find it has diminished or become compressed into just half its original volume. Adding more mercury until the difference in level is 60 inches, thus subjecting the air to 3 atmospheres pressure, we find the volume reduced to $\frac{1}{3}$; whilst at 90 inches or 4 atmospheres the volume is $\frac{1}{4}$.

Thus, pressures	1,	2,	3,	4	(atmospheres)
give volumes	1,	$\frac{1}{2}$,	$\frac{1}{3}$,	$\frac{1}{4}$,	

or the volume is inversely proportional to the pressure.

Gradually letting out mercury at D, we notice the volume of air gradually increases. Beginning at 90 inches with $\frac{1}{4}$ vol., at 60 inches we get $\frac{1}{3}$, at 30 inches $\frac{1}{2}$, at 15 inches $\frac{2}{3}$, and at 10 inches $\frac{3}{4}$, whilst at the level at B (if our stopcock C has been perfectly tight) we again obtain the original volume of air; in diminishing the pressures the volumes were

Volumes	$\frac{1}{4}$,	$\frac{1}{3}$,	$\frac{1}{2}$,	$\frac{2}{3}$,	$\frac{3}{4}$,	1,
Pressures	4,	3,	2,	$\frac{3}{2}$,	$\frac{4}{3}$,	1 (atmospheres).

Exactly the same results would have followed if instead of air we had taken hydrogen, oxygen, or nitrogen.

This experiment illustrates *Boyle's Law*, which states that *when the temperature is constant the volume of a gas is inversely proportional to the pressure.* But it only proves it for pressures greater than that of the atmosphere.

It also follows from Boyle's Law and from the above experiments that *the density of a gas is directly proportional to the pressure to which it is subjected.*

EXPT. 23.—To prove the law for lower pressures than that of the atmosphere, the apparatus shown in Fig. 30 must be employed. It consists of a long tube full of mercury, at the top of which is a glass dish, also containing mercury. A tube, closed at one end, and about 5 feet long, is filled with mercury except about 6 inches, the end is firmly closed with the thumb and inverted in the glass mercury trough. The tube is now depressed in the trough until the mercury is at the same level inside and outside the tube, the contained air is then at the ordinary pressure say 30 inches, a little strip of paper is gummed to mark the volume of air, and the tube raised until the volume is doubled; it will then be seen

that the mercury has risen 15 inches. The total pressure at the level of the mercury in the trough is 30 inches, and as we have mercury in the tube equal to 15, the gas must press with a force equal to another 15, making 30, or the pressure of the gas is found by subtracting the height of the mercury column (measured from the level in the trough) from the height of the barometer observed at the time. $30 - 15 = 15$ or $\frac{1}{2}$ an atmosphere. If it is now raised until we have 3 times the volume, we find our column at 20 inches, so pressure is $30 - 20 = 10$ or $\frac{1}{3}$ an atmosphere. Similarly, when we have 4 volumes the pressure is $30 - 22\frac{1}{2} = 7\frac{1}{2} = \frac{1}{4}$ atmosphere. Again we have

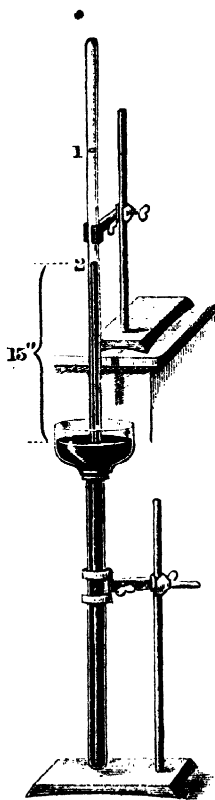


Fig. 30.

Pressures 1, $\frac{1}{2}$, $\frac{1}{3}$, $\frac{1}{4}$ (atmospheres),
Volumes 1, 2, 3, 4.

Boyle's Law is not correct for any gas under very high pressures or in the case of gases which are near their point of liquefaction (see p. 63).

Calculation of the Volumes of Gases at different Pressures.—Suppose it is desired to find the volume of a gas at a pressure of 785 mm. which at 735 mm. measures 478 c.c. From Boyle's Law we know that the volumes are inversely proportional to the pressures, and, therefore, in the ratio of 785 : 735. So the volume will be $\frac{478 \times 735}{785}$ c.c. It is easily remembered whether to multiply by the higher or lower number, by asking, Is the volume increased or diminished? If the pressure is diminished the volume is increased, and we must multiply by the higher and divide by the lower number and *vice versâ*.

Calculation of the Volumes of Gases at different Temperatures and Pressures.—Making both corrections at the same time, we may wish to find, for example, the volume of hydrogen at NTP (normal temperature and pressure, 0° C. and 760 mm.), which at 15° and 780 mm. measures 587 c.c.

$$\frac{587 \times 273}{288} \times \frac{780}{760}, \text{ or}$$

$$\frac{587 \times 273 \times 780}{288 \times 760} = \text{vol. of hydrogen at NTP.}$$

It will be noticed that the gas is cooled, and its volume therefore tends to diminish, and that the pressure is lowered, and therefore its volume tends to increase.

Relations between the Densities of Gases and their Atomic and Molecular Weights.—It has been found, taking the density of hydrogen as 1, that *the numbers expressing the densities of the gaseous elements are identical with their atomic weights,* whilst the density of any compound gas is half its molecular weight.* We shall afterwards find that the *molecule* of the elementary gases consists of *two* atoms. The general statement is, therefore, as follows: *the density* (H = 1) *of any gas (elementary or compound) is half its molecular weight.*

Elementary Gases.	Formula.	Atomic Weight.	Molecular Weight.	Density.
Hydrogen	H_2	1.0	2.0	1.0
Oxygen	O_2	15.9	31.8	15.9
Nitrogen	N_2	13.9	27.8	13.9
Chlorine	Cl_2	35.2	70.4	35.2

Compound Gases.	Formula.	Molecular Weight.	Density
Water	H_2O	17.9	8.95
Nitrogen Monoxide	N_2O	43.7	21.85
Carbon Monoxide	CO	27.8	13.90
Carbon Dioxide	CO_2	43.7	21.85

Calculation of Volumes of Gases at any Temperature and Pressure, from a given Weight of Gas.—We have already learnt that hydrogen is the lightest gas

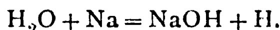
* There are certain exceptions to this law which will be noticed later, *e.g.* phosphorus and arsenic have four atoms to the molecule, mercury has only one, and the density of phosphorus and arsenic is double the atomic weight, whilst that of mercury is only half.

known, and that it is taken as the standard with which to compare the densities of all the other gases. It has been found by careful experiment that *a litre of hydrogen at NTP weighs* 0.0899 *gram.* It is evident that the weight of a litre of any gas is proportional to its density, and therefore a litre of oxygen at NTP weighs 0.0899 gram × 15.9, and a litre of nitrogen at NTP weighs 0.0899 × 13.9, because oxygen is 15.9 times, and nitrogen 13.9 times as heavy as hydrogen, whilst a litre of carbonic acid gas at NTP weighs 0.0899 × 21.85 (grms.). If a litre of hydrogen weighs 0.0899 grm., it is easily calculated that 2 grms. of hydrogen occupy 22.247 litres (say 22.25 or 22¼ litres), therefore

2	grams	(or 1 × 2)	of hydrogen	occupy	22.25	litres
31.8	,,	(15.9 × 2)	,, oxygen	,,	22.25	,,
27.8	,,	(13.9 × 2)	,, nitrogen	,,	22.25	,,
70.4	,,	(35.2 × 2)	,, chlorine	,,	22.25	,,
43.7	,,	(21.85 × 2)	,, carbon dioxide	,,	22.25	,,

In other words, the molecular weight (in grams) of any gas occupies 22.25 litres.

Examples.—(1) What volume of hydrogen at 15° and 740 mm. will be given off by adding 4 grms. of sodium to water?



$$H_2O + Na = NaOH + H.$$

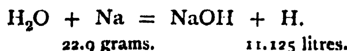
Directions.—First Method.

(1) Find the weight (w) of hydrogen given off (see p. 34). $\frac{1 \times 4}{22.9} = w.$

(2) Find the volume (v) at NTP corresponding to w. $\frac{w \times 1000}{.0899}$ = volume in cubic centimetres (NTP) $= v$.

(3) Find the volume corrected to the required temperature and pressure. $= \frac{v \times 288 \times 760}{273 \times 740} = V$ the vol. sought.

Second Method.—A shorter method than the foregoing may be carried out as follows, depending upon the fact that the molecular weight of a gas (in grams) occupies 22.25 litres; or, the atomic weight (in grams) of an elementary gas, such as hydrogen, oxygen, chlorine, occupies 11.125 litres.



$$H_2O + Na = NaOH + H.$$

22.9 grams. 11.125 litres.

In the foregoing equation we may take it, therefore, that 22.9 grams of sodium yield 11.125 litres of hydrogen (NTP). Then by reduction to unity; if 22.9 yield 11.125 litres, 1 yields $\frac{11.125}{22.9}$, and 4 yield, therefore, $\frac{11.125 \times 4}{22.9}$, or $\frac{44.5}{22.9}$ litres at NTP; this volume must then be corrected to 15° and 740 mm. by the method already given.

(2) What volume of carbon dioxide CO_2 at 5° and 680 mm. will be given off by burning 15 grams of carbon? $C + O_2 = CO_2$.

$$\frac{43.7 \times 15}{11.9} = w \qquad \frac{w \times 1000}{.0899 \times 21.85} = v \qquad \frac{v \times 278 \times 760}{273 \times 680} = V \text{ (in c.c.'s)}.$$

$$\underset{11.9 \text{ grams.}}{C} + O_2 = \underset{22.25 \text{ litres.}}{CO_2}.$$

The above equation may be read that 11.9 grams of carbon yield 22.25 litres of CO_2 at NTP, then we have by reduction to unity $\frac{22.25 \times 15}{11.9}$, the required volume at NTP, which must be corrected to 5° and 680 mm.

Calculation of Weights from Volumes of Gas at any Temperature and Pressure.—It must always be remembered that dividing the weight of any gas by $0.0899 \times d$ (where d is its density) gives its volume *at NTP*, and this volume must then be corrected for any other temperature and pressure. On the other hand, when it is required to find the weight of any volume of gas at any temperature and pressure other than NTP, its vol. must first be converted to NTP *before* proceeding to find the weight, *e.g.* :—

(3) What weight of carbon is contained in 4.78 litres of carbon dioxide measured at 15° C. and 660 mm.?

Directions.—First Method.

(1) Find vol. at NTP. $\frac{4.78 \times 273 \times 660}{288 \times 760} = v$ (litres at NTP).

(2) Find weight of gas. $v \times .0899 \times 21.85 = w$ (in grams).

(3) Find weight of carbon. $\frac{11.9 \times w}{43.7} = W$, weight of carbon.

Second Method.—After reducing to NTP, we may proceed thus:

22.25 litres of CO_2 (NTP) correspond to 11.9 grams of carbon, then by reduction to unity we have

$$22.25 \text{ litres } CO_2 \text{ equal } 11.9 \text{ grams of C.}$$

$$1 \quad ,, \quad ,, \quad \frac{11.9}{22.25} \quad ,,$$

$$v \quad ,, \quad ,, \quad \frac{11.9 \times v}{22.25} \quad ,,$$

where v is the volume of CO_2 in litres reduced to NTP.

What we have learnt

In our seventh Lesson we have considered Dalton's Law, which states that all gases expand very nearly $\frac{1}{273}$ part of their volume at 0° for every increase in temperature of 1° C., and also the method of converting gaseous volumes from one temperature to another. The relations of the volume of gases to pressure has been studied; it was seen that all changes in volume and pressure conform to Boyle's Law, which states that the volume of any gas is inversely proportional to the pressure to which it is subjected. We have seen how the law may be proved for pressures both above and below that of the atmosphere, and also how to calculate gaseous volumes from one temperature and pressure to any other. The relations between the molecular weights of gases and their densities have been considered, as also has the method of calculating the volumes of gases from their weights, and *vice versâ*.

Exercises on Lesson VII

1. What is Dalton's Law? Convert 869 vols. of gas at 14° C. to 5° C.
2. What is a Torricellian vacuum? How can you prove it does not contain any gas?
3. How would you demonstrate Boyle's Law both for pressures above and below that of the atmosphere?
4. Convert (*a*) 278 c.c. of gas at 3° C. and 640 mm. to 16° C. and 780 mm.; (*b*) 1000 c.c. of gas at 0° and 760 mm. to 15° C. and 720 mm.
5. What weight of oxygen is contained in 10 litres of carbon dioxide measured at 12° C. and 770 mm.?
6. What volume of carbon dioxide at 20° C. and 725 mm. will be given off from 560 grams of marble, $CaCO_3$, which is completely decomposed by heat into lime, CaO, and carbon dioxide, CO_2.
7. Calculate the density of the following gaseous bodies: ozone, O_3, hydrochloric acid, HCl, sulphuretted hydrogen, H_2S, ammonia, NH_3. What is the weight of 10 litres of ammonia gas at NTP?
8. What weight of sulphur must I burn in order to generate 60 litres of sulphur dioxide, SO_2, at 20° and 760 mm.?

LESSON VIII

PHYSICAL PROPERTIES OF GASES—*Continued*

RELATIONS BETWEEN THE COMBINING VOLUMES OF GASES—AVOGADRO'S LAW—DIFFUSION, LIQUEFACTION, AND SOLIDIFICATION OF GASES.

Avogadro's Law.—Since the densities of the elementary gases are indicated by their atomic weights (p. 55), it follows that *equal volumes of any of the elementary gases contain the same number of atoms at the same temperature and pressure.* This law may be extended to include all gases, since the density of any gas is half its molecular weight, and we may say, therefore, that *equal volumes of any of the gases, elementary* or compound contain the same number of molecules* † (*at the same temperature and pressure*). This is known as Avogadro's Law, which was enunciated by him in 1811 on purely physical grounds connected with the identical behaviour of chemically different gases towards changes of temperature and pressure. Since equal volumes of different gases contain the same number of molecules it follows that the molecule of any gas, simple or compound, occupies the same volume as a molecule of hydrogen. In other words, *the molecule of any gas occupies two volumes.*

Relations between the combining Volumes of Gases.—Gay-Lussac in 1808 discovered the Law, known by his name, of the relation between the combining volumes of gases, viz. that *the volumes in which gaseous substances combine, bear*

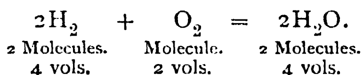
* The molecules of elementary gases are usually composed of *two* atoms.

† The molecule of a compound is the smallest group of its component atoms which can exist in the free state, hence the molecule of a compound cannot be divided without decomposing it.

a simple relation to one another, and to the volume of the resulting product. This Law is in accordance with Avogadro's Law, and was discovered experimentally before the latter Law was known.

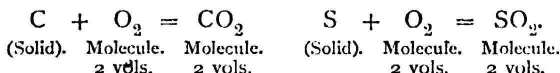
Taking a few examples of the simple relations between the combining volumes of gases, it has been found by actual experiments, which will be considered under their respective headings, that

(1) When four volumes of hydrogen and two volumes of oxygen combine together to form water vapour *as steam*, a contraction takes place and *four* volumes of steam are produced (see p. 94).



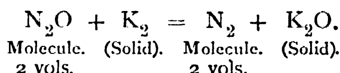
$2H_2$	+	O_2	=	$2H_2O$.
2 Molecules.		Molecule.		2 Molecules.
4 vols.		2 vols.		4 vols.

(2) When carbon or sulphur is burnt in oxygen in a closed vessel no increase in the volume of the gas is observed (see p. 203).



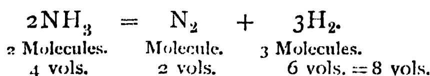
C	+	O_2	=	CO_2		S	+	O_2	=	SO_2.
(Solid).		Molecule.		Molecule.		(Solid).		Molecule.		Molecule.
		2 vols.		2 vols.				2 vols.		2 vols.

(3) When nitrogen monoxide N_2O is decomposed by means of potassium, which combines with and absorbs the oxygen and sets the nitrogen free, no change of volume takes place (see p. 155).



N_2O	+	K_2	=	N_2	+	K_2O.
Molecule.		(Solid).		Molecule.		(Solid).
2 vols.				2 vols.		

(4) When ammonia gas (NH_3) is decomposed by means of the electric spark, its volume is doubled (see p. 166).



$2NH_3$	=	N_2	+	$3H_2$.
2 Molecules.		Molecule.		3 Molecules.
4 vols.		2 vols.		6 vols. = 8 vols.

In all these cases we find that the deductions which we have made from theory are confirmed by actual facts obtained by experiment.

Diffusion of Gases.—Döbereiner first noticed in 1823

that when a flask which happened to have a fine crack in it was filled with hydrogen over water, and then allowed to stand, the volume of the hydrogen was found next day to have become much less. The same diminution did not take place if the cracked flask was covered with a bell-jar containing hydrogen, nor did it take place if the flask was filled with air. Graham, in 1832, first showed that air entered the flask when hydrogen left it, but in the first case, hydrogen passed out or diffused through the crack *faster* than air entered, whilst in the second case hydrogen was able to enter or diffuse into the cracked vessel just as fast as it diffused out, and no alteration of bulk was to be noticed.

EXPT. 24.—This power of the molecules of gases to diffuse through very fine apertures is best illustrated by means of the following experiment. A cylindrical porous cell, such as is used for voltaic batteries, is fitted with an india-rubber stopper pierced with a hole into which a long glass tube is fixed. The tube has a bulb and U tube ending in a jet (Fig. 31), and is filled with a coloured liquid before the experiment, whilst the porous cell contains air. If now a beaker full of hydrogen is brought over the porous cylinder, it will be found that the coloured liquid is thrown up as a fine fountain, showing that the pressure in the porous cell is increased. The reason is, that the hydrogen diffuses or passes through the pores of the porous cell *much faster* than the air diffuses out of it.

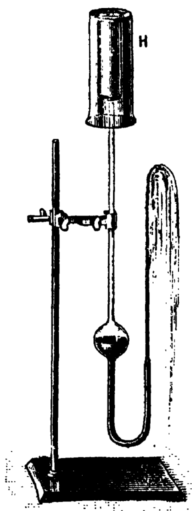


Fig. 31.

EXPT. 25.—If we arrange the apparatus rather differently (as in Fig. 32), so as to surround the porous cell (containing air) with the heavy gas carbon dioxide, we shall find that the air passes out of the porous cell more rapidly than the carbon dioxide diffuses into it; the pressure is thereby diminished and air passes from the inlet tube, through the water and into the porous cell, to supply the deficiency.

EXPT. 26.—If we take two small gas jars with ground and well-fitting mouths, place them together (Fig. 33), and render them air-tight by rubbing vaseline over the ground surfaces, we might expect, at first sight, that if the upper jar is completely filled with hydrogen (density = 1), and the lower one with carbon dioxide (density = 22), two gases which do not combine with each other, then the heavy gas would *remain* in the lower jar and the light gas in the upper one. But this is not found to be the case. Our previous experiments on diffusion would prepare us for the observed fact that, *in two communicating vessels containing different gases, no matter what their relative densities, diffusion takes place until an equilibrium is established, and then both vessels contain an identical mixture of the two gases.* If we try the experiment, and leave the two gases in contact, as shown in Fig. 33, for a few hours, then slipping a circular glass plate over the mouth of each jar, invert them over a strong solution of caustic potash, we shall find that the liquid rises half-way up each jar, showing that both jars contain an equal mixture of carbonic acid gas (which is absorbed by caustic potash), and hydrogen (which remains unabsorbed).

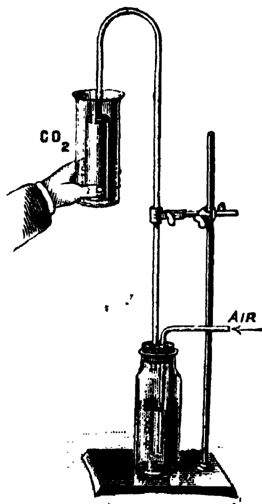


Fig. 32.

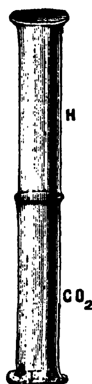


Fig. 33.

EXPT. 27.—Another experiment, showing the rapid diffusion of gases, may be easily made as follows. A gas jar is inverted in a retort stand ring, and filled with hydrogen by upward displacement (see p. 72). Another jar (not inverted) is filled with carbonic acid gas by downward displacement (see p. 225). The two jars are allowed to remain open in a room of equable temperature and free from draughts for a few hours. When a lighted taper is introduced into

both jars it continues to burn in each as in air. In fact both jars are now full of ordinary air. Both the hydrogen and the carbonic acid have diffused into the atmosphere.

Law of Diffusion.—Graham found that *the relative rates of diffusion of gases are inversely proportional to the square roots of their densities.*

Hence hydrogen will diffuse four times as fast as oxygen, for $\frac{1}{\sqrt{1}} : \frac{1}{\sqrt{16}} :: 4 : 1$. In Expt. 27 if we had ascertained the times taken for the gases to diffuse from the jars, we should have found that the hydrogen diffused away much more rapidly than the carbon dioxide. The following table gives the rate of diffusion of several gases, as experimentally determined by Graham, compared with the inverse square roots of their densities.

	DENSITY. Air = 1.	$\frac{1}{\sqrt{\text{Density}}}$.	VELOCITY OF DIFFUSION. Air = 1.
Hydrogen	0.06926	3.7790	3.830
Nitrogen	0.97130	1.0150	1.014
Oxygen	1.10560	0.9510	0.949
Carbon dioxide	1.52900	0.8087	0.812

showing that the numbers found by experiment agree closely with those calculated from the law.

The diffusion of gases is of very great importance in the economy of nature, for by this means the air of towns and dwellings is kept in a pure condition, the vitiated and foul air constantly diffusing into large volumes of purer air. Diffusion, however, is only secondary to the action of winds and ventilation * in the renewal of the pure air which we require for breathing.

Liquefaction of Gases.—We have seen in our first lesson that all gases may be condensed to liquids by the combined influence of cold and pressure. Some substances which are gases at the ordinary temperature may be condensed to liquids at the ordinary atmospheric pressure by means of cold alone, whilst at 0° these gases may be condensed to liquids by pressure alone, as shown in the following table.

* See p. 145 for an account of ventilation.

		Cold Alone. (Pressure 760 mm.)	Pressure Alone. (Temperature, 0° C.)
Sulphur dioxide	SO_2	− 10°	1.53 Atmospheres
Chlorine	Cl	− 34°	6 ,,
Sulphuretted hydrogen	H_2S	− 62°	10.8 ,,
Ammonia	NH_3	− 40	4.40 ,,
Carbon dioxide	CO_2	− 80	38.50 ,,
Nitrous oxide	N_2O	− 92	32 ,,

Critical point in the Liquefaction of Gases.—The case of carbon dioxide is very instructive, because it is found impossible to liquefy that gas by pressure alone if the temperature is higher than a certain limit. Above this temperature, if the gas be compressed until a pressure of about 72 atmospheres is reached, no liquefaction takes place, but if now the tube containing the compressed gas be gradually cooled, we find that at the temperature 31°.35 the gas becomes disturbed and cloudy and separates into a layer of liquid carbonic acid, which is sharply distinguished from the gas above. If now the temperature be raised above 31°.35, the liquid appears to lose its sharp surface and the tube is filled with a cloudy mass in commotion and soon nothing is visible, the liquid having become entirely vaporised. This temperature (31°.35) is called the *critical temperature* of liquefaction for carbon dioxide. Above it the gas cannot be liquefied, no matter how great the pressure. There are similar but not identical critical temperatures for all gases. The so-called *permanent* gases such as oxygen, hydrogen, nitrogen, were for a long time considered to be non-liquefiable, simply because pressure was brought to bear upon them at temperatures higher than the critical point. We now know that their critical points are far below the freezing point (0°), and by excessive cold as well as great pressure they have been obtained as liquids.

Heat produced when Gases are compressed.—This is very well shown by means of a strong glass tube fitted with a light piston. When the tube is full of air and the piston forced inwards so as to compress the air, heat is evolved which is sufficient to inflame a small piece of tinder moistened with ether, which is inserted into a cavity at the end of the piston.

Cold produced when Gases expand.—Conversely when gases expand, heat is absorbed or cold produced. This

absorption of heat is sufficient to cause the solidification of carbonic acid gas when the liquid is run out from a strong iron bottle through a fine jet into a brass box. Part of the liquid vaporises at once, and the heat absorbed in its conversion from liquid to gas is so great as to *solidify* the remaining liquid. Solid carbon dioxide is a snow-like mass and is often used for obtaining very low temperatures.

Mixed with ether and placed in the vacuum of an air-pump its evaporation produces a temperature of $-100°$ C.

WHAT WE HAVE LEARNT

In our eighth Lesson we have considered Avogadro's Law, which states that equal volumes of any of the gases contain, at the same temperature and pressure, the same number of molecules.

We have seen that a very simple relation exists between the combining volumes of gases, and that the molecule of any gas occupies the same space (2 volumes) as the molecule (2 atoms) of hydrogen.

The diffusion of gases has been demonstrated and the law of diffusion discovered by Graham has been given. We have learnt something more about the liquefaction and solidification of gases, and noticed the influence of temperature near the *critical point*.

EXERCISES ON LESSON VIII

1. What is Avogadro's Law? From what experimental facts is it deduced?

2. What can be deduced from Avogadro's Law as regards the relations between the combining volumes of gases?

3. What volume of chlorine will be required to completely decompose 10 litres of sulphuretted hydrogen, H_2S [$Cl_2 + H_2S = 2HCl + S$ (solid)], and what volume of hydrochloric acid gas, HCl, will be formed?

4. How would you demonstrate the diffusion of hydrogen and carbon dioxide through the walls of a porous cell containing air?

5. What is meant by the *critical point* in the liquefaction of gases? Give an example. Why were nitrogen and oxygen considered to be *permanent* gases?

6. How may carbon dioxide be solidified?

7. State Graham's law of the diffusion of gases.

8. How was the diffusion of gases discovered?

9. Give examples of the simple relations existing between the combining volumes of gases.

PART II

SYSTEMATIC STUDY OF CERTAIN NON-METALLIC ELEMENTS, AND THEIR MORE IMPORTANT COMPOUNDS.

LESSON IX

Hydrogen

SYMBOL H. ATOMIC WEIGHT 1. DENSITY 1

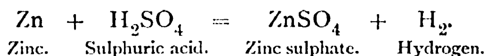
CAVENDISH in 1766 first ascertained the true nature of this gas, to which he gave the name of inflammable air.

Occurrence.—Hydrogen occurs almost solely in a state of combination in nature, though it sometimes exists in the free state mixed with other gases in certain volcanic emanations. Its principal compound is water, H_2O, of which it forms one-ninth part by weight. As all the oceans, seas, rivers, and lakes on the face of the earth contain one-ninth their weight of hydrogen, the quantity of this element occurring in a state of combination is very large. Hydrogen also forms an essential ingredient of all animal and vegetable bodies, and most organic compounds (*e.g.* sugar, starch, fat, wax, etc.) contain it as a constituent. All mineral oils contain a large proportion of hydrogen combined with carbon.

Test for Hydrogen.—Hydrogen may be recognised by the fact that if brought in contact with a flame, it burns with a

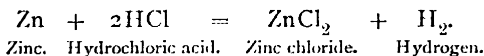
pale lambent blue flame, and, if burnt in a dry jar, bedews the sides of the vessel with moisture, owing to its combination with oxygen (in the air) to form water, whilst if lime-water be subsequently added, no precipitate is produced as would be the case if the gas had been a carbon compound, some of which burn similarly.

Preparation.—(1) The usual method of preparing hydrogen is by the action of dilute sulphuric or hydrochloric acid on metallic zinc;*the chemical reactions are—



$$Zn + H_2SO_4 = ZnSO_4 + H_2.$$

Zinc. Sulphuric acid. Zinc sulphate. Hydrogen.



$$Zn + 2HCl = ZnCl_2 + H_2.$$

Zinc. Hydrochloric acid. Zinc chloride. Hydrogen.

Expt. 28.—Into the flask (Fig. 34) a quantity of granulated zinc is introduced. The flask is fitted with an india-rubber stopper pierced with two holes. Into one of these is fitted a long thistle funnel, reaching nearly to the bottom of the flask, and into the other a bent delivery tube passes just beneath the stopper, and thence beneath the bee-hive shelf of the pneumatic trough, and serves for the delivery of the gas into the gas jar, which is first filled with water. Having arranged the apparatus, the dilute acid is poured down the thistle funnel so as to cover the zinc to a depth of one or two inches. The liquid soon begins to effervesce, from the evolution of hydrogen gas. Here a most important **caution** must be given to prevent accidents. Beginners, when making this experiment, must remember that *hydrogen gas and common air form a highly explosive mixture;* and that, as the flask is filled with air, the gas which first comes off is a

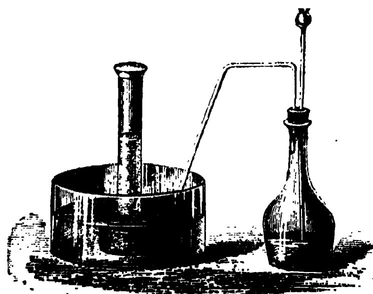


Fig. 34.

* The metal magnesium is sometimes used when the hydrogen is required to be pure.

mixture, which, if collected in a gas jar and a light applied, will explode violently. Therefore we must, *before beginning to make any experiments with hydrogen, be quite sure that no air is mixed with it.* To ensure this we have only to wait several minutes until the hydrogen, which is quickly evolved, has driven out the air. We can easily learn whether this has taken place, and whether the gas is ready for collecting, by placing a test-tube filled with water, and inverted, over the little hole in the bee-hive shelf. When the tube is full of gas it must be removed, with the thumb closing its mouth, and held mouth downwards to a flame. If the gas burns with a slight explosion, or does not burn at all, the gas is still

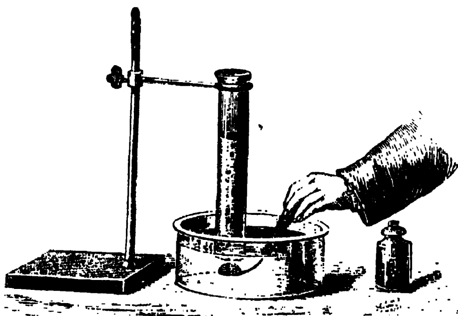


Fig. 35.

mixed with air, and we must wait a little longer; and if after a short time the trial is again made, and the gas burns quietly, the gas is free from air and may be collected for further experiments (Experiment 44, p. 96, shows the explosive nature of a mixture of hydrogen and oxygen).

(2) Iron filings may be used instead of zinc, but the gas thus evolved is not so pure owing to impurities in the iron. The reaction is similar to that which occurs when zinc is used.



$$Fe + H_2SO_4 = FeSO_4 + H_2.$$

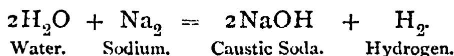
Iron. Sulphuric acid. Ferrous sulphate. Hydrogen.



$$Fe + 2HCl = FeCl_2 + H_2.$$

Iron. Hydrochloric acid. Ferrous chloride. Hydrogen.

(3) By the action of sodium * on water (Fig. 35 ; see also Experiment 11, p. 14),

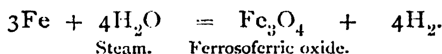


$$2H_2O + Na_2 = 2NaOH + H_2.$$

Water. Sodium. Caustic Soda. Hydrogen.

The hydrogen obtained in this manner generally burns with a bright yellow flame owing to the presence of traces of sodium hydroxide.

(4) By the action of water as steam on red-hot iron,



$$3Fe + 4H_2O = Fe_3O_4 + 4H_2.$$

Steam. Ferrosoferric oxide.

Water is boiled in a small flask, and the steam passes into an iron or porcelain tube filled with iron borings heated to

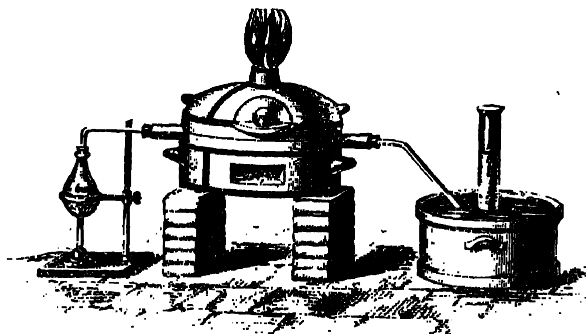
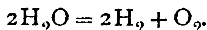


Fig. 36.

redness in the furnace (Fig. 36). The oxygen of the water (steam) combines with the iron to form the black oxide of iron, Fe_3O_4 (magnetic oxide of iron, or ferrosoferric oxide), whilst the liberated hydrogen passes on into a gas jar.

(5) By the electrolysis of acidulated † water (Fig. 37 ; see also Experiment 12, p. 15),



$$2H_2O = 2H_2 + O_2.$$

* Potassium also decomposes water in a similar manner, but the action is more violent and the heat evolved is sufficient to set fire to the gas, which burns with a violet flame owing to the presence of potassium hydroxide.

† A little sulphuric acid is added to enable the water to conduct the current of electricity.

Properties.—Hydrogen is a colourless, invisible, tasteless, and inodorous gas, and is the lightest substance known, and for this reason it is taken as the standard with which to compare the density or heaviness of all the other gases. Hence at the head of this lesson we find Density = 1, or the density of hydrogen is taken as unity. The density of common air at NTP is 14.39, whilst the density of carbonic acid gas is 21.85. In other words, air is nearly $14\frac{1}{2}$ and carbonic acid nearly 22 times as heavy as hydrogen. A litre of hydrogen at NTP weighs 0.0899 grams. This number should always be remembered, because, knowing the density of any gas, the weight of a litre of it is obtained by multiplying 0.0899 by the density.

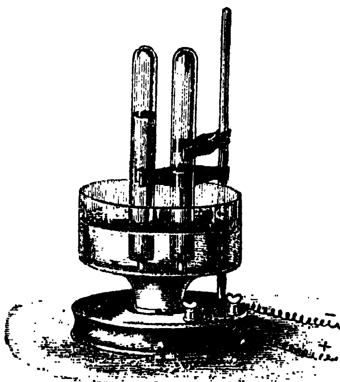


Fig. 37.

Experiments with Hydrogen

EXPT. 29. **Hydrogen a very light Gas.**—(1) Collect a jar of the gas and pour it upwards into a similar inverted dry gas jar, Fig. 38 (see also Experiments 2 and 3, p. 1. The light gas there mentioned is hydrogen). The light hydrogen ascends to the top of the jar and drives out the air before it as it gradually fills the jar. A lighted taper brought to the mouth of the jar will ignite the gas with a slight explosion, because in pouring the gas upwards it has become mixed with a little air. Notice that the previously dry sides of the gas jar become bedewed with moisture, showing that when hydrogen burns in air it produces *water*.

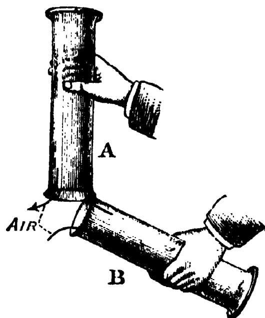


Fig. 38.

Expt. 30. **Hydrogen may be collected by Upward Displacement.**—(2) The bent delivery tube in the generating apparatus is replaced by an upright one passing to the top of an inverted gas jar (Fig. 39). The light gas collects at the top and displaces the heavier air. That the jar is full of hydrogen may be shown by lighting the gas at the mouth of the jar. If after collecting the gas by upward displacement it be lighted at the jet, and a cold bell-jar be held over the flame, it will be seen that the inside of the bell-jar becomes bedewed with moisture, which gradually collects into small drops of liquid water.

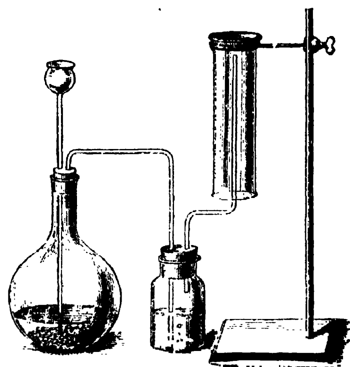


Fig. 39.

Expt. 31. **Soap Bubbles blown with Hydrogen ascend.**—(3) The gas is passed through a U tube filled with cotton wool, and the delivery tube is connected by means of a piece of india-rubber tubing to a thistle funnel, which is placed in a soap solution * so as to blow bubbles. On breaking away they ascend in the air and rise to the ceiling where they burst. Light collodion balloons when filled with hydrogen rise in the air.

Expt. 32. **Hydrogen is an Inflammable Gas but does not support Combustion.**—(4) Into an inverted jar of hydrogen plunge a small lighted taper fastened on the end of a piece of wire. The flame will set fire to the hydrogen at the mouth of the jar, but will itself be extinguished when raised into the gas. On withdrawing the taper it again takes fire on coming in contact with the burning gas near the mouth; plunged upwards it again goes out, and may be extinguished and re-

* The soap solution for these experiments is best prepared by dissolving 10 grams of sodium oleate in 400 c.c. of cold distilled water; 100 c.c. of pure glycerine are then added, and the mixture well shaken. After allowing to stand in the dark for a few days, the clear solution is siphoned off, and a drop of strong ammonia added. It should be kept in the dark and not exposed to the air.

lighted many times by moving it into and out of the gas. This shows that both the hydrogen and the taper only burn when in contact with the air. Hydrogen cannot directly combine with the materials of the taper (carbon and hydrogen), and the flame is therefore extinguished in that gas.

WHAT WE HAVE LEARNT

In our ninth Lesson we have learnt the principal methods of preparing hydrogen and the most important of its properties. It may be made, *e.g.* (1) by the action of sulphuric or hydrochloric acid on zinc or iron; (2) from water, (*a*) by electrolysis, (*b*) by the action of sodium or potassium, or (*c*) by the action of red-hot iron on steam. Its principal properties were seen to be its lightness and inflammability, and its want of power to support combustion in the ordinary manner like air. Hydrogen is a colourless, invisible, inodorous gas. Gaseous water or steam is produced when hydrogen burns in air. Hydrogen can be collected by the upward displacement of air.

EXERCISES ON LESSON IX

1. Describe two methods of preparing hydrogen, give equations for the reactions, and sketch the apparatus you would use.
2. What precautions must you take in showing experiments with hydrogen?
3. What volume of hydrogen at 14° and 735 mm. will be evolved on dissolving 40 grams of zinc, (1) in sulphuric acid, (2) in hydrochloric acid? If the same weight of iron is used instead of zinc what volume of gas will be evolved?
4. What weight of water will be produced on burning all the hydrogen given off in (3)?
5. What volume of oxygen at 16° and 750 mm. will be required to burn all the hydrogen in (3)?
6. Describe several experiments which illustrate the principal properties of hydrogen.
7. What is the action of steam on red-hot iron?
8. What weight of iron is contained in 60 grams of ferrosoferric oxide?
9. In making hydrogen I obtained 60 grams of zinc sulphate; what weight of zinc was dissolved?
10. Why is a burning taper extinguished when plunged into a jar of hydrogen?
11. How would you distinguish between hydrogen and carbon-monoxide, a gas which, like hydrogen, burns with a pale blue flame in air?

LESSON X

OXYGEN AND THE OXIDES
HYDROXIDES, ACIDS, BASES, AND SALTS

Oxygen

SYMBOL O. ATOMIC WEIGHT 15.9. DENSITY 15.9

PRIESTLEY, in England, discovered oxygen on the 1st of August, 1774, when he heated oxide of mercury by means of the sun's rays concentrated by a burning glass. It was afterwards discovered independently by Scheele, in Sweden in 1775.

Occurrence.—Of all the elements which occur on our planet, oxygen, either free or combined, is the most widely diffused and is found in the largest quantity. Oxygen occurs in the free state in the atmosphere, of which it forms one-fifth by volume. And, in combination with hydrogen, it forms $\frac{8}{9}$ of the total weight of water on the earth's surface. It occurs very plentifully in a state of combination in all rocks, and is an essential constituent in all animal and vegetable structures.

Test for Oxygen.—Oxygen gas may be recognised by the fact that if a splinter of wood, which has only a glowing spark on it, be plunged into the gas, it immediately bursts into flame owing to the rapid combustion. (Nitrous oxide, N_2O, also answers this test, but we shall learn to distinguish it on p. 158.)

Preparation.—(1) Oxygen is generally obtained in the laboratory by decomposing potassium chlorate, $KClO_3$, which,

at a temperature of about 350°, decomposes into potassium chloride and oxygen.

EXPT. 33.—The apparatus used is shown in Fig. 40. The white crystalline salt is strongly heated in a flask by means of a Bunsen burner. It first melts and then begins to give off bubbles of gas, which soon come off briskly. The degree of heat must be carefully regulated, or the decomposition becomes so violent that the collection of the gas is

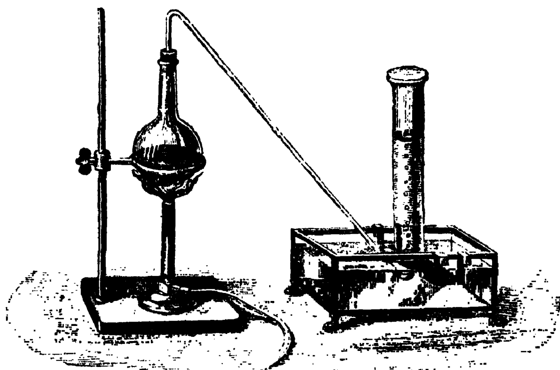


Fig. 40.

difficult, and sometimes the flask is burst. The following equation represents the reaction—



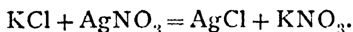
$$2KClO_3 = 2KCl + 3O_2.$$

For this reaction a high temperature is required, and if the flask is not of hard glass * it often melts before the decomposition is finished.

That the chloride remaining is a different substance from the chlorate can be demonstrated by dissolving a little of each in distilled water and adding a few drops of silver nitrate solution, $AgNO_3$. The chlorate is unaltered, but the chloride

* Hard glass contains potash in place of soda and is much less easily melted, hence it is used in cases where it has to withstand a very high temperature.

gives a white curdy precipitate of silver chloride, AgCl, which is insoluble in nitric acid. This is a test for a chloride.



$$KCl + AgNO_3 = AgCl + KNO_3.$$

EXPT. 34.—(2) In order to obtain the gas at a lower temperature, a small quantity of manganese dioxide is mixed with the powdered chlorate; the gas then comes off at 200° C. before the salt fuses. The manganese dioxide is not altered during the chemical reaction and may be recovered unchanged. The part it plays is not thoroughly understood.

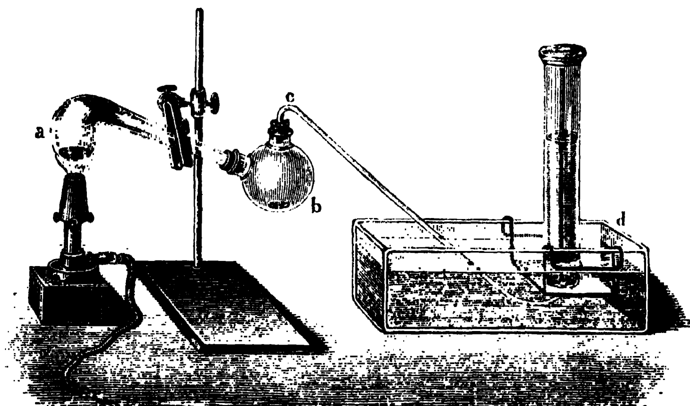
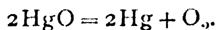


Fig. 41.

(3) Oxygen may be obtained by strongly heating mercuric oxide, which decomposes into metallic mercury and oxygen.



$$2HgO = 2Hg + O_2.$$

The oxide is strongly heated in the retort (Fig. 41), when the liquid metal collects in the receiver, whilst the oxygen is collected over water in the pneumatic trough (see also second part of Experiment 10, p. 9).

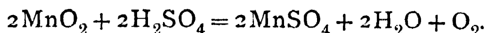
(4) Manganese dioxide loses a portion of its oxygen when heated strongly, thus



$$3MnO_2 = Mn_3O_4 + O_2.$$

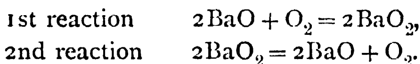
The pure dioxide is placed in an iron bottle and heated to bright redness, when $\frac{1}{3}$ of its oxygen escapes in the gaseous state.

(5) Manganese dioxide also gives off oxygen when heated in a glass flask with strong sulphuric acid,



$$2MnO_2 + 2H_2SO_4 = 2MnSO_4 + 2H_2O + O_2.$$

(6) **Preparation of Oxygen from the Air.***—Oxygen is now used in large quantities for the production of the oxy-hydrogen light or lime-light, and is prepared in a very interesting manner from the air. The method depends upon the fact that baryta, BaO, or oxide of barium, takes up oxygen from the air at a dull red heat, but the dioxide, BaO_2, thus formed is decomposed again at a bright red heat into baryta and free oxygen, thus



1st reaction $2BaO + O_2 = 2BaO_2$,
2nd reaction $2BaO_2 = 2BaO + O_2$.

The baryta can be used over and over again. Instead, however, of using two temperatures to bring about the desired reactions, it is found that the combination of the baryta and oxygen takes place when air is pumped over the heated baryta under pressure, nitrogen passing off; whilst, if the retort containing the heated baryta be afterwards exhausted by an air-pump, the dioxide decomposes under the lower pressure, the temperature remaining the same. In this way the oxygen absorbed from the air is pumped out of the retort, and after storing in a large gas-holder, is forced under very great pressure into strong steel cylinders for transport. The amount of oxygen which the cylinders contain is proportional to the pressure under which the gas is forced into them. Owing to their small bulk, they are very convenient for the transportation of oxygen from place to place, and the gas can be used gradually, as required, by turning a small stopcock. In order to prevent the gas rushing out with great force on opening the stopcock, a

* Oxygen is now separated from the atmosphere by this method on a large scale by Brin's Oxygen Company of London; they also separate and compress the residual nitrogen.

regulator is employed by the aid of which a gentle stream of oxygen can be obtained.

(7) Oxygen may also be obtained from many other substances containing large quantities of that element, such as lead dioxide, PbO_2, chromium trioxide, CrO_3, potassium manganate, K_2MnO_4, bleaching powder (which contains calcium hypochlorite, $CaCl_2O_2$), sulphuric acid, H_2SO_4, etc.*

Properties.—Oxygen is a colourless, invisible, tasteless, and inodorous gas. It is slightly heavier than atmospheric air, having a specific gravity of 1.10493 (air = 1) or 15.9 when hydrogen is taken as the unit. A litre of oxygen at NTP therefore weighs 0.0899 × 15.9 grams or 1.42941 grams. Oxygen is the great supporter of combustion, and bodies which burn in air (which contains only one-fifth its volume of oxygen, the rest being inert nitrogen) burn much more brilliantly in oxygen.

Combustions in Oxygen

EXPT. 35. **Phosphorus.** — We may define a combustion as an act of chemical combination accompanied by the evolution of light and heat. Several gas jars of oxygen having been collected, a small piece of phosphorus,† about the size of a pea, is carefully placed in a cold brass deflagrating spoon which is held a little distance over a small Bunsen flame until it melts and takes fire. It is then at once plunged into a jar of oxygen, when a most vivid combustion of the phosphorus begins, an intensely white light being emitted and dense fumes of solid phosphorus pentoxide being produced; these, however, soon dissolve in water and are absorbed if a layer of water be left in the gas jar on collecting the gas (see Expt. 9, p. 8). If a little blue litmus solution is now added to the water in the gas jar after the fumes have subsided, it is at once turned red, showing that an acid (phosphoric acid, H_3PO_4) has been produced.

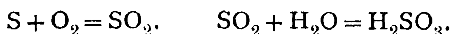


$$P_4 + 5O_2 = 2P_2O_5. \qquad P_2O_5 + 3H_2O = 2H_3PO_4.$$

EXPT. 36. — **Sulphur** in the same way burns with a

* See under sulphuric acid (p. 212). † See footnote, p. 8.

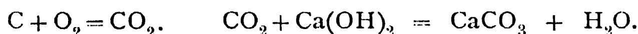
bright blue flame, brighter than in air, producing a gas called sulphur dioxide, SO_2, which dissolves in water, as in the previous experiment, forming sulphurous acid, H_2SO_3.



$$S + O_2 = SO_2. \qquad SO_2 + H_2O = H_2SO_3.$$

The presence of an acid can be shown by litmus as before.*

EXPT. 37. — **Carbon** or charcoal, which burns very slowly and with a dull flame in air, burns brightly and with brilliant scintillations in oxygen,† forming carbon dioxide, CO_2. If a little lime-water be introduced into the gas jar after the combustion of carbon, it is at once turned milky owing to the formation of a white insoluble substance (calcium carbonate, $CaCO_3$).



$$C + O_2 = CO_2. \qquad CO_2 + Ca(OH)_2 = CaCO_3 + H_2O.$$

EXPT. 38. **Iron.**—A bundle of fine iron wire or a steel watch spring can easily be burnt in oxygen, if tipped with burning sulphur and plunged into the gas. The oxide of iron formed (Fe_3O_4) drops down in the molten state and cracks the gas jar, unless a little sand or a layer of water is placed in the bottom to prevent it.

EXPT. 39. **Hydrogen. The Oxy-Hydrogen light or Lime-light.** — When hydrogen (or, more generally, coal gas) is burnt in a stream of oxygen in a specially constructed burner (Fig. 42), an intensely hot but very feebly luminous flame is produced. If, however, the flame be allowed to impinge upon a cylinder of lime, that substance becomes heated to such a high temperature that it becomes incandescent and gives off a brilliant and dazzling white light. This is made use of in the magic lantern, and also in public entertainments where a brilliant illumination is desired.

"Supporter of Combustion" and "Combustible Body," only relative Terms.—It has been said that oxygen is a *supporter of combustion*, and that hydrogen is a *combustible*

* Lavoisier gave the name oxygen to this gas (from ὀξύς, acid, γεννάω, I produce) because of this production of acid.

† A piece of bark charcoal shows the scintillations best.

body, but a little consideration will show us that these terms are only relative, *e.g.* if our rooms could be filled with hydrogen (or coal gas) and our gas pipes could be filled with oxygen (or air), we could turn on the oxygen at a gas jet, and by applying a light obtain a flame of oxygen burning in hydrogen. This would seem to reverse the ordinary state of things, for the oxygen would then be the combustible body, and the hydrogen the supporter of combustion. As a matter of fact, however, neither of the gases has either name rightly applied to it, because *both* are necessary to the chemical action which results in flame. It is by the chemical combination of the *two* substances that the heat and light are produced, and neither is

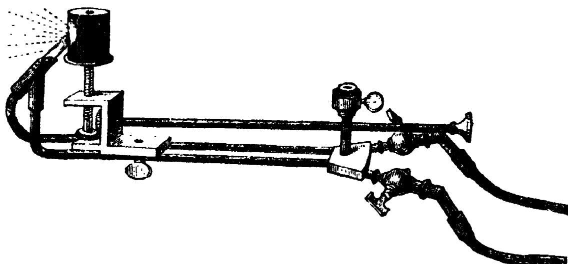


Fig. 42.

more essential than the other for the production of the effect. Yet, as in everyday life we speak of a substance that will burn in air as a combustible body, it is convenient to call oxygen a supporter of combustion.

EXPT. 40.—A simple experiment will illustrate this subject and make it quite clear. We will fill an inverted gas jar with hydrogen, and light the gas at the mouth of the cylinder; we will now immediately plunge a glass tube into the gas from which is issuing a slow stream of oxygen from a Brin's oxygen cylinder furnished with a regulator, and we shall find that as the jet of oxygen is thrust up through the burning hydrogen, it takes fire and burns. We saw in Lesson IX. under hydrogen, that a lighted taper thrust up into that gas was extinguished, because the materials of the taper (carbon and hydrogen) had no power of combining directly with hydrogen, but oxygen has

this power, and therefore it burns, or, more correctly, the two gases burn together.

This experiment may be made more simply with coal gas instead of hydrogen. Common air may also be substituted for oxygen by delivering it slowly from a blow-pipe bellows.

The Oxides

All the elements, with the single exception of fluorine, are found to unite with or form compounds with oxygen, which are termed oxides. These may generally be placed in one of the following three classes, (1) basic oxides, (2) acid-forming oxides, (3) peroxides. The oxides and hydroxides of metals are usually *basic*, whilst the oxides of non-metals usually form acids on combination with water.

Hydroxides.—Most of the oxides combine with water to form hydroxides, or hydrated oxides, *e.g.*—

(1) Basic Oxides.					Basic Hydroxides (called Bases).	
Sodium oxide	Na_2O	+	H_2O	=	$2NaOH$	Caustic soda.
Potassium oxide	K_2O	+	H_2O	=	$2KOH$	Caustic potash.
Calcium oxide	CaO	+	H_2O	=	$Ca(OH)_2$	(Lime-water and slacked lime).
Barium oxide	BaO	+	H_2O	=	$Ba(OH)_2$	Baryta water.
Ferric oxide	Fe_2O_3	+	$3H_2O$	=	$Fe_2(OH)_6$	Ferric hydroxide.

(2) Acid-forming Oxides.*					Hydroxides (called Acids).	
Sulphur dioxide	SO_2	+	H_2O	=	H_2SO_3	Sulphur*ous* acid.
Sulphur trioxide	SO_3	+	H_2O	=	H_2SO_4	Sulphur*ic* acid.
Phosphorus trioxide	P_2O_3	+	$3H_2O$	=	$2H_3PO_3$	Phosphor*ous* acid.
Phosphorus pentoxide	P_2O_5	+	$3H_2O$	=	$2H_3PO_4$	Phosphor*ic* acid.
Carbon dioxide	CO_2	+	H_2O	=	H_2CO_3	Carbon*ic* acid.
Nitrogen trioxide	N_2O_3	+	H_2O	=	$2HNO_2$	Nitr*ous* acid.
Nitrogen pentoxide	N_2O_5	+	H_2O	=	$2HNO_3$	Nitr*ic* acid.

Basic Oxides (or Hydroxides), when they are soluble in water, turn red litmus blue, feel soapy to the skin, and all of them neutralise acids to form *salts*.

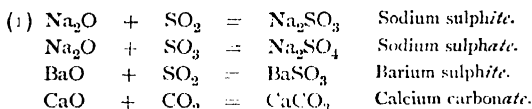
Acid-forming Oxides are oxides which combine with water to form acids.

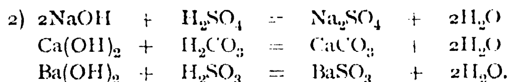
Acids turn blue litmus red, have a sharp, sour taste, and neutralise basic oxides and hydroxides, forming salts. They

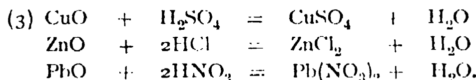
* Sometimes called *anhydrides* or the anhydrides of the acids. Anhydride means *without water*.

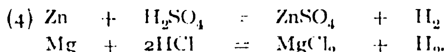
may be considered as hydrogen salts or salts in which the metal is replaced by an equivalent of hydrogen.

Salts.—Basic and acid-forming oxides combine together to form an important class of bodies called *salts*. Salts may be formed either (1) by the simple combination of an acid-forming and a basic oxide, or (2) by the combination of the corresponding hydroxides, in which case water is eliminated, or (3) by the combination of basic oxides and acids, or (4) by the displacement of hydrogen from acids by metals, *e.g.*—


(1) $Na_2O + SO_2 = Na_2SO_3$ Sodium sulph*ite*.
$Na_2O + SO_3 = Na_2SO_4$ Sodium sulph*ate*.
$BaO + SO_2 = BaSO_3$ Barium sulph*ite*.
$CaO + CO_2 = CaCO_3$ Calcium carbon*ate*.


(2) $2NaOH + H_2SO_4 = Na_2SO_4 + 2H_2O$
$Ca(OH)_2 + H_2CO_3 = CaCO_3 + 2H_2O$
$Ba(OH)_2 + H_2SO_3 = BaSO_3 + 2H_2O$.


(3) $CuO + H_2SO_4 = CuSO_4 + H_2O$
$ZnO + 2HCl = ZnCl_2 + H_2O$
$PbO + 2HNO_3 = Pb(NO_3)_2 + H_2O$.


(4) $Zn + H_2SO_4 = ZnSO_4 + H_2$
$Mg + 2HCl = MgCl_2 + H_2$.

Salts may be considered as acids in which the hydrogen has been replaced wholly or in part by a metal, and we notice that metals, such as Na and K, replace hydrogen atom for atom—these are called *monad* or *monovalent* elements; but in the case of such metals as Ca, Ba, Zn, one atom of the metal replaces *two* atoms of hydrogen—these are called *dyad* or *divalent* elements.

Nomenclature of Acids and Salts

will be noticed that both the oxides of sulphur form acids, and the names of the two acids and their salts are examples of the general rule that the name of an acid produced from a *lower oxide* ends in "*ous*" and its salts in "*ite*," whilst the *higher oxide* gives rise to an acid the name of which ends in "*ic*" and its salts end in "*ate*," *e.g.*—

N_2O_3	forms	Nitr*ous*	acid and	Nitr*ites*.
N_2O_5	,,	Nitr*ic*	,,	Nitr*ates*.
SO_2	,,	Sulphur*ous*	,,	Sulph*ites*.
SO_3	,,	Sulphur*ic*	,,	Sulph*ates*.
P_2O_3	,,	Phosphor*ous*	,,	Phosph*ites*.
P_2O_5	,,	Phosphor*ic*	,,	Phosph*ates*.

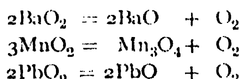
Acids the names of which begin with "*hydro*" and end in "*ic*" form salts the names of which terminate in "*ide*"; thus we have

HCl, *Hydro*chlor*ic*	acid forms	Chlor*ides*.
HBr, *Hydro*brom*ic*	,,	Brom*ides*.
HF, *Hydro*fluor*ic*	,,	Fluor*ides*.
H_2S, *Hydro*sulphur*ic*	,,	Sulph*ides*.

Neutralisation.—Salts usually do not either turn red litmus blue, or blue litmus red, *i.e.* they are *neutral*, but important exceptions will be met with hereafter.

EXPT. 41.—If we take a solution of caustic soda and add a solution of red litmus to it, the colour is immediately changed to blue. If now we add a small quantity of acid (say sulphuric acid), insufficient to combine with all the caustic soda, no change of colour is observed. If we then continue the addition of acid we come at last to a point at which the colour is neither blue nor red. The solution is then said to be *neutral*, and the *base* is said to be *neutralised* by an *acid*. At this point there is neither free caustic soda nor free sulphuric acid, but a solution of sodium sulphate. Any further addition of acid will now change the litmus to red. Litmus is called an *indicator*, because it indicates whether a substance is acid, neutral, or alkaline.*

Peroxides.—These usually contain more oxygen than the other two classes, a portion of which is given off on heating, *e.g.* the following *di*-oxides—

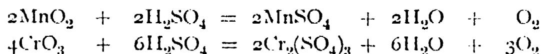


$$2BaO_2 = 2BaO + O_2$$
$$3MnO_2 = Mn_3O_4 + O_2$$
$$2PbO_2 = 2PbO + O_2$$

On treating peroxides with sulphuric acid, they usually decompose, a portion of the oxygen being liberated, and the

* The same experiment can be performed with the basic (or basylous) oxide, Lime, CaO, or its hydrate, $Ca(OH)_2$, and hydrochloric acid, water being eliminated.

residual basic oxide combines with the acid to form a salt, water also being eliminated, *e.g.*—



$$2MnO_2 + 2H_2SO_4 = 2MnSO_4 + 2H_2O + O_2$$
$$4CrO_3 + 6H_2SO_4 = 2Cr_2(SO_4)_3 + 6H_2O + 3O_2$$

If hydrochloric acid is used, however, chlorine may be liberated, *e.g.*—



$$MnO_2 + 4HCl = MnCl_2 + 2H_2O + Cl_2.$$

This classification is not a perfect one, because some oxides can act either as acid-forming or basic oxides, according to the body with which they combine, but these must be studied under the head of metals. Other oxides have neither acid nor basic properties: *e.g.* H_2O, N_2O, NO, etc.

WHAT WE HAVE LEARNT

In our tenth Lesson we have learnt the various methods of preparing oxygen (and particularly on the large scale from the air by Brin's process), its principal properties and uses, and the method adopted for its storage and transport. The true meaning of the term "supporter of combustion." Oxides and hydroxides, basic and acid-forming oxides, peroxides, bases, acids, and salts, neutralisation and the use of litmus, and the nomenclature of acids and salts have been considered.

EXERCISES ON LESSON X

1. Describe two methods of preparing oxygen, give equations and sketches of apparatus.
2. How is oxygen prepared from the air? How is it stored and used?
3. Describe experiments to prove that oxygen is a supporter of combustion, show that this term is only relative.
4. What weight of oxygen can be obtained by heating 50 grams of MnO_2? What will be its volume at 13° and 720 mm.?
5. Give examples of basic and acid-forming oxides and hydroxides. What happens when these bodies are brought together?
6. What is meant by neutralisation? give two examples.
7. Give the names and formulæ of the acids and the potassium salts derived from SO_2, SO_3, N_2O_3, N_2O_5, P_2O_3, P_2O_5.
8. How would you distinguish between a chloride and a chlorate?
9. How did Priestley obtain oxygen gas?
10. What compounds are formed when (1) basic oxides, (2) acid-forming oxides are dissolved in water?

LESSON XI

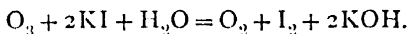
Ozone

PREPARATION—PROPERTIES AND COMPOSITION

FORMULA O_3. MOLECULAR WEIGHT 47.7. DENSITY 23.85

ANY one who has worked an electrical machine knows that a peculiar smell accompanies the electrical discharge from a pointed conductor. This smell is due to the formation, in the air, of a body called Ozone, hence its name from ὄζειν to smell.

Test for Ozone.—Ozone possesses remarkably energetic properties, hence it is sometimes called "active oxygen." This is shown by holding near the point of discharge a piece of filter paper moistened with a colourless solution of boiled starch to which a few crystals of potassium iodide (KI) have been added, when we observe that a deep blue colour is produced. This is due to the oxidising action of the ozone, by which iodine is liberated, and the free iodine forms a deep blue compound with the boiled starch. This chemical action may be represented as follows—



$$O_3 + 2KI + H_2O = O_2 + I_2 + 2KOH.$$

This reaction is used as a test for ozone.

EXPT. 42. **Ozone contains Nothing but Oxygen and is Decomposed by Heat.**—Perhaps the above-noted effects may be caused by some other gas besides oxygen present in the air. Let us, therefore, make the experiments with pure and dry oxygen and see whether we get the same results. Here is a glass tube (Fig. 43) through which pure dry

oxygen is passing, and so arranged that the gas can be subjected to the influence of an electric discharge. As the gas issues from the tube, whilst under the electrical influence, we notice the same smell as before, and our starch and iodide paper is at once turned blue. So we find that ozone can be obtained from pure dry oxygen, and it therefore contains no other element but oxygen. More than this, if we attach a piece of glass tube to the end of that from which ozone is issuing, and heat it with a Bunsen burner, we will see that the starch paper is no longer turned blue nor can any smell of ozone be perceived. Evidently, then, ozone is destroyed by heat.

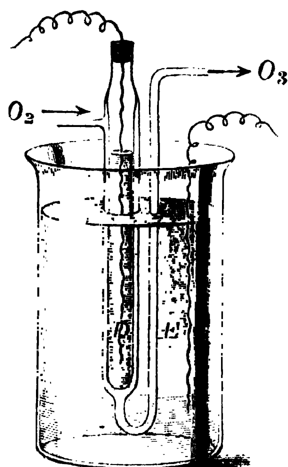


Fig. 43.

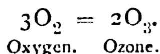
(1) **Preparation.** — Ozone is best prepared by passing pure dry oxygen through the annular space between two glass tubes (one inside the other); the inner tube contains dilute sulphuric acid, in which hangs a platinum wire connected with one pole of an induction coil in action, whilst the outer tube is placed in a beaker also containing dilute sulphuric acid, which is connected with a wire from the other pole of the coil, as shown in Fig. 43.

(2) Ozone is also produced in the electrolytic decomposition of water, especially if the electrodes consist of fine platinum wire. If the oxygen given off is allowed to impinge upon "starch paper," the blue colour is at once produced. If electrolytic oxygen is perfectly dried, it still retains its smell of ozone, and on heating, it decomposes without the formation of water, showing that the compound contains no hydrogen (it was at one time supposed that this compound was H_2O_3, but the above experiment disproves it).

(3) Ozone is also produced when phosphorus is allowed to hang, at a suitable temperature, in a flask containing moist air.

Properties.—Ozone is a gas possessing a peculiarly characteristic smell (resembling very dilute chlorine), whence its name. It can be condensed to a blue liquid, and is a very powerful oxidising agent. In its oxidising actions its volume undergoes no alteration, as a molecule of ozone produces a molecule of free oxygen, the other atom being used for the oxidation. Ozone produces a characteristic effect on mercury, taking away its lustre and mobility, destroying the convexity of its surface, and making it adhere to glass as a thin mirror. Its action on potassium iodide has already been mentioned. It oxidises phosphorus to phosphoric acid, H_3PO_4, in presence of moisture, sulphides to sulphates, and it has a strong oxidising action on all organic matter.

Composition of Ozone.—It is now known that ozone is a peculiar modification or "allotropic condition" of oxygen, due to a rearrangement of the atoms in the molecules, such that 3 molecules of oxygen ($3O_2$), each containing two atoms, are rearranged so as to produce 2 molecules of ozone ($2O_3$) each containing three atoms, thus—



$$\underset{\text{Oxygen.}}{3O_2} = \underset{\text{Ozone.}}{2O_3}.$$

Experimental determination of the Composition of Ozone.—For many years the exact composition of ozone remained unknown. It was at one time supposed to be a compound of hydrogen and oxygen, H_2O_3, but its formation from pure dry oxygen as well as the fact that no water is produced on decomposing ozone by heat show that this is incorrect.

(1) **Ozone is Condensed Oxygen.**—When a silent electric discharge is passed through pure dry oxygen contained in a glass tube furnished with two platinum wires, fused into the glass and ending in a bent capillary tube in which some strong sulphuric acid is placed (Fig. 44), it is seen that a gradual diminution of volume occurs, the column of sulphuric acid (upon which the ozone does not act) being drawn up towards the bulb tube.

This diminution of bulk has never been seen to be greater than $\frac{1}{12}$ of the volume of the oxygen (only a small proportion of the oxygen being converted into ozone).

(2) **Ozone Expands when Decomposed by Heat.**—

Having now converted as much as is possible of the oxygen into ozone, let us fuse up the end of the capillary U tube, and heat the bulb containing the ozone to a temperature of 300° C., and after allowing the vessel to cool to the original temperature, we will open the sealed end of the U tube and we find that the volume is exactly what it was before the ozonisation, *i.e.* during the formation of ozone, oxygen is condensed, and during its decomposition by heat, it regains its original volume. Moreover, as we have seen (Expt. 42), the ozone is entirely decomposed by heat.

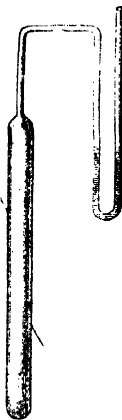


Fig. 44.

(3) **Ozone is Absorbed by Turpentine without Decomposition.**—Certain oils, such as oil of turpentine, have the power of absorbing ozone without decomposing it, and it is found that *the volume of ozone absorbed by the oil is exactly double the diminution in volume noticed when the oxygen was ozonised. It is also exactly double the increase of volume noticed when the ozone is decomposed by heat.*

Hence supposing that we ozonise oxygen and have a contraction of, say, 1 volume, and if we now absorb the ozone by turpentine, we shall have a further contraction of 2 volumes or a total contraction of 3 volumes. Hence 3 volumes of oxygen (total contraction) are condensed to form 2 volumes (absorbed by turpentine) of ozone.



$$3O_2 = 2O_3,$$

therefore the formula of ozone is O_3.

(4) **Ozone Destroyed by Potassium Iodide suffers no change in Volume.**—When a sealed bulb containing a solution of potassium iodide is introduced into the ozone tube (Fig. 44) before ozone is produced, it is found after converting the oxygen into ozone until no further diminution of volume occurs that if the bulb be then broken and iodine liberated, *no further change in the volume of the gas is noticed;* whilst if the amount of the iodine liberated be exactly determined, and the volume of oxygen corresponding to it be calculated, it is found that the volume of oxygen absorbed

by potassium iodide is exactly equal to the diminution in bulk on ozonisation.

All the above experiments are explained by the formula O_3 for ozone.

(1) Oxygen contracts when ozonised.

$$(6 \text{ vols.})\ 3O_2 = 2O_3\ (4 \text{ vols.})\ \text{decrease 2 vols.}$$

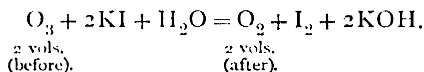
(2) The *expansion* of ozonised oxygen on decomposing it by heat is *equal to* the *contraction* on ozonising.

$$(4 \text{ vols.})\ 2O_3 = 3O_2\ (6 \text{ vols.})\ \text{increase 2 vols.}$$

(3) The diminution on ozonising and the increase on decomposing by heat is *exactly half* the volume absorbed by turpentine.

Decrease and increase (above equations 1 and 2) = 2 vols.
Volume absorbed by oil is $2O_3$ = 4 vols.

(4) The volume of ozonised oxygen is *unchanged* when the ozone is decomposed by potassium iodide.



$$\underset{\substack{\text{2 vols.}\\ \text{(before).}}}{O_3} + 2KI + H_2O = \underset{\substack{\text{2 vols.}\\ \text{(after).}}}{O_2} + I_2 + 2KOH.$$

(5) **Confirmation of Formula by the Density Determined by Rate of Diffusion.**—Another very ingenious experiment has proved that the formula O_3 is correct. We have learnt on p. 63 that the relative rates of diffusion of two gases are inversely proportional to the square roots of their densities. Evidently, then, if we can find the rate of diffusion of ozone compared with the rate of diffusion of chlorine (of known density), we can easily calculate the density of ozone. This has been done, and it is found that the density of ozone is 23.85 or $1\frac{1}{2}$ times that of oxygen, and therefore the formula is O_3.

What we have learnt

In our eleventh Lesson we have learnt the various methods of preparing ozone and some of its most characteristic properties. We have seen that it is composed of nothing but oxygen, which is in a condensed state, such that three volumes of ordinary oxygen are condensed to 2 volumes of

"active oxygen" or ozone, which is only an allotropic modification of oxygen. The composition of ozone was determined by various experimental methods and found to be O_3, which formula is confirmed by the rate of diffusion of the gas.

Exercises on Lesson XI

1. How may ozone be best prepared?

2. What are the most characteristic properties of ozone? How would you test for ozone?

3. Discuss the reasons for giving the formula O_3 to ozone.

4. I have 670 c.c. of oxygen containing .4 per cent of ozone at NTP, what will be the volume of the gas after heating to 300°, and cooling to 15.5° and 780 mm.?

5. What weight of iodine will be liberated from potassium iodide by 250 c.c. of oxygen containing, at NTP, 2 per cent of ozone?

6. A litre of oxygen at NTP, containing an unknown volume of ozone liberated .0468 grams of iodine, what is the volume of the ozone and what percentage of ozone does the oxygen contain?

7. How may the composition of ozone be confirmed by a determination of its rate of diffusion?

8. Give an equation showing the action of ozone upon potassium iodide.

LESSON XII

Compounds of Hydrogen and Oxygen



H_2O and H_2O_2

WATER (HYDROGEN MONOXIDE)—DETERMINATION OF ITS CHEMICAL COMPOSITION BY EUDIOMETRIC AND GRAVIMETRIC SYNTHESIS, AND BY ELECTROLYSIS—HYDROGEN DIOXIDE.

Water

FORMULA H_2O. MOLECULAR WEIGHT 17.9. VAPOUR DENSITY 8.95

PURE water is a clear tasteless liquid, colourless when seen in moderate quantity, but when viewed in bulk, possessing a bluish-green colour. This blue colour may be observed by looking at a white plate which has been lowered into a deep clear lake, or by looking at it through a column of distilled water about 6 to 8 metres in length, contained in a tube with blackened sides and plate-glass ends.

Chemical Composition of Water

Cavendish's Experiments.—In the introductory lessons we found that we could obtain the two gases hydrogen and oxygen from water, hydrogen by means of sodium and both gases by electrolysis. It was also seen that when hydrogen burns in air water is produced.

Up to the close of last century, water was considered to be

an element. It was in 1781 that Henry Cavendish first made an exact synthesis of water and ascertained its chemical composition. He made very careful experiments to determine the proportions in which oxygen and hydrogen combine by volume. An apparatus similar to that used by him is shown in Fig. 45. It consists of a very strong pear-shaped glass globe A, fitted with two wires B, for the purpose of passing an electric spark through the gases contained in it.

It is fitted also with a stopcock, and it can be exhausted of air by the air-pump and screwed on the top of the glass gas cylinder. Cavendish introduced into the gas cylinder two parts of hydrogen and one part of oxygen by volume. On opening the stopcock the mixed gases enter the exhausted globe, and after closing the stopcock they are fired by a spark. He found that after the spark was passed, all the gas disappeared (or "lost its elasticity") and the globe again became vacuous whilst the inside was coated with a film of dew, which was simply water vapour condensed to the liquid state.

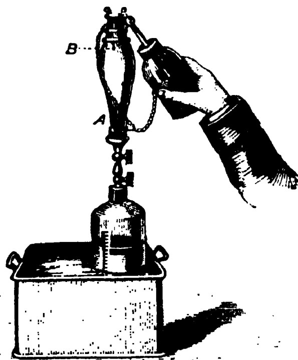


Fig. 45.

After the first charge had been fired, the globe could be again filled with gas by opening the stopcock, without a fresh exhaustion, and the experiment repeated until all the gas in the cylinder had entered the globe. In this manner Cavendish proved that two volumes of hydrogen and one volume of oxygen unite together to form water, which was found to have neither taste nor smell, and left no sensible sediment when it was evaporated to dryness,—in short it was pure water.

Eudiometric Synthesis of Water.—The principle which Cavendish used is still employed, but the modern methods of carrying out the experiments are much more accurate. The pear-shaped globe is replaced by a long glass tube of uniform bore, closed at one end [illegible] a *eudiometer*

(A) Fig. 46. Near the closed end two platinum wires are fused through the glass for the purpose of passing a spark. The tube is graduated in millimetres throughout its length for the purpose of reading off the exact height of the mercury above the level of that in the trough, which is furnished with plate-glass sides. The eudiometer is first filled completely with mercury and inverted in the glass trough, pure oxygen is then introduced, and the volume, temperature, and pressure accurately read off. Then an excess of hydrogen is added, and the data read off as before. Next the eudiometer is pressed firmly down on a pad of india-rubber fixed at the bottom of the trough and under the mercury, and a spark is passed. On releasing the eudiometer the volume of gas is found to have diminished, and all the oxygen has disappeared together with exactly twice its volume of hydrogen. For the purpose of ascertaining the temperature of the gases, a thermometer is hung near the eudiometer, and an interval of rest is allowed between each reading so as to allow the whole apparatus and the air of the room to reach an equable temperature. The pressure to which each volume of gas is subjected is found by reading the height of the barometer and subtracting the height of the column of mercury in the eudiometer above the level of that in the trough; for it is evident that when at rest the pressure inside the eudiometer at the level of the mercury in the trough is equal to the atmospheric pressure shown by the barometer, but this is made up of the pressure of the gas and the pressure of mercury in the eudiometer, and therefore by subtracting the latter, which can be easily read off, we obtain the pressure of the gas. The volumes of the gases at

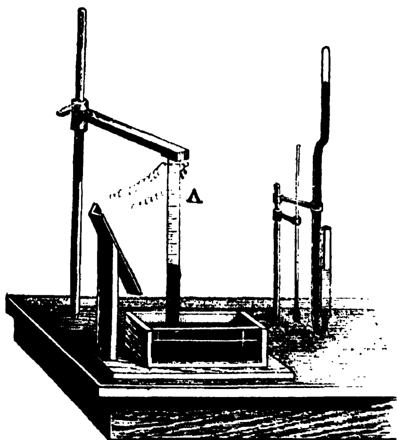


Fig. 46.

each reading being known they are reduced to 0° and 760 mm. NTP (normal temperature and pressure) before beginning further calculations. The volume of liquid water produced is almost inappreciable; a correction can, however, be made for it, and also for the tension of aqueous vapour (see p. 105).

To render this clear let us suppose that the amount of oxygen was 50 vols. at NTP, and that of hydrogen, 150 vols, and that after passing the spark a residual 50 vols. at NTP consisting of pure hydrogen was found, then it is evident that all the oxygen 50 vols. has combined with 150 – 50 = 100 vols. of hydrogen; or the ratio of oxygen to hydrogen by volume is 1 : 2.

Volumetric Composition of Steam by Synthesis.—Gay-Lussac was the first to ascertain that two volumes of hydrogen and one volume of oxygen combine together to form two volumes of gaseous steam. This can be proved by means of the apparatus shown in Fig. 47. It consists of a eudiometer tube, which is surrounded by a wider glass tube or jacket, through which can be passed a current of vapour of amyl alcohol (which boils at 132° C.) from the flask in which the liquid is boiled, the object of this being to keep, in the state of vapour, the whole of the water which is formed by the union of the oxygen and hydrogen. The vapour of the amyl alcohol passes out and condenses in the flask placed in cold water. The eudiometer is joined to another plain tube open at the top, the whole forming a U tube which has a branch tube at the side for the inlet and outlet of mercury, thus enabling the pressures to be adjusted by raising or lowering the mercury reservoir. A mixture of exactly two volumes of hydrogen and o[illegible] of oxygen, obtained in the apparatus shown in Fig. 49, is first [illegible]ssed into the eudiometer and its temperature raised to 132° [illegible]neans of the amyl alcohol vapour. The mercury in both [illegible] is adjusted

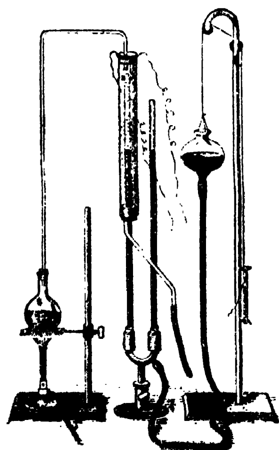


Fig. 47.

:o the same level and the volume read off, after which the pressure is reduced and a spark passed. Combination takes place, and it is found, on again adjusting the pressures, that the volume of gaseous water produced (measured at the same temperature, viz. 132°) is exactly $\frac{2}{3}$ of that of the original mixture, showing that two volumes of hydrogen and one of oxygen combine to form two volumes of gaseous steam, a *contraction* of $\frac{1}{3}$ of the bulk of the uncombined gases taking place after combination.

EXPT. 43. **Volumetric Analysis of Water.**—Fig. 48 shows the apparatus which may be used for the electrolytic decomposition of water. The bulb and the straight tube are filled with acidulated water, which, on opening the two stopcocks at the

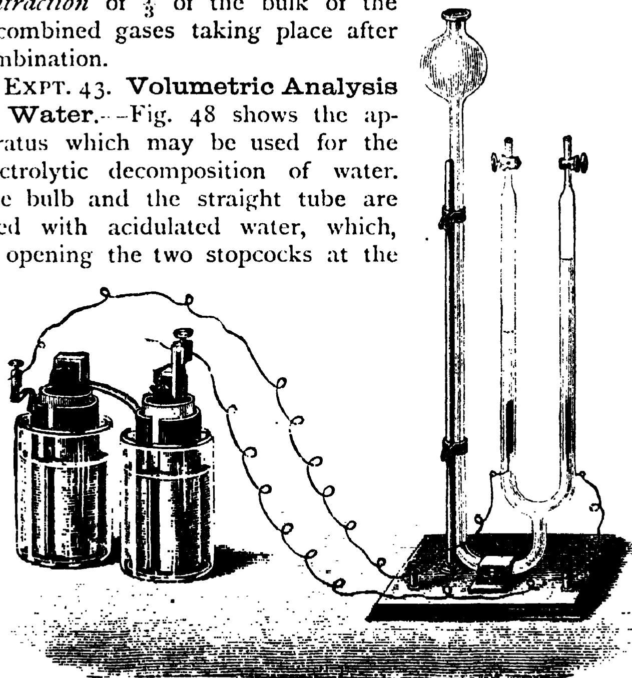
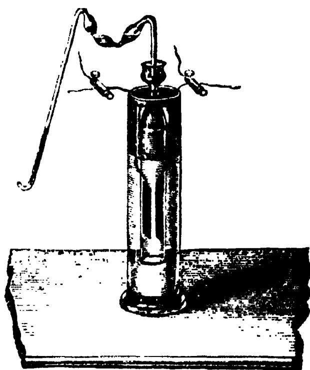


Fig. 48.

end of the U tubes, rises and fills the gas collecting tubes. A current of electricity from a battery is then passed through the liquid by means of the two platinum wires fused through the two tub forming the U. The platinum wires terminate in platin... ...tes or *electrodes*, from which, on joining up the connecting w... a constant stream of minute bubbles of gas

rises, oxygen from the + and hydrogen from the – electrode, and the gases collect separately in the stoppered tubes.

It will be noticed that the volume of oxygen given off is rather less than half that of the hydrogen; and the reason is that (1) oxygen is more soluble in water than hydrogen and a portion remains dissolved, and (2) a little ozone is formed which occupies less space and is more soluble than oxygen. That the larger volume of gas is hydrogen may be shown by opening the stopcock, when the pressure of liquid in the bulb-tube forces the gas out and it may be lighted and observed to burn with the characteristic flame of hydrogen. The other gas ignites a glowing chip and is oxygen. That the gas contains ozone may be demonstrated by allowing the issuing gas to impinge against an iodised starch paper (see ozone, p. 85), which is turned blue. By raising the temperature of the acidulated water to 100° the solubility of the oxygen is diminished, whilst that of the hydrogen remains practically unchanged, and at the same time the formation of ozone is avoided, so that the true volume relation is thus more closely attained.


Fig. 49.

Electrolytic Gas.—This is the name given to the mixture of hydrogen and oxygen in the proportion 2 : 1, produced in the electrolysis of water, when they are collected together. Fig. 49 shows a form of apparatus used for making electrolytic gas, which explains itself.

EXPT. 44. **Experiments with Electrolytic Gas.**—When electrolytic gas is brought in contact with a flame or electric spark, combination takes place with explosive violence, owing to the sudden *expansion* of the gaseous steam produced by the great *heat* evolved in the act of chemical combination. This is best shown by collecting a small flask of electrolytic gas, and fitting it on an india-rubber stopper pierced with two holes, through which pass two stout copper wires terminating in small pieces of platinum wire not quite in contact. The

flask is supported as shown in Fig. 50, and covered with a wire gauze covering. When a spark from an induction coil is passed, a loud explosion takes place which shatters the flask to fine dust.

Soap bubbles may be blown with electrolytic gas, and as they ascend they may be touched with a lighted taper, giving rise to a loud explosion. Care must, however, be taken that the light does not come in contact with the end of the tube which delivers the explosive gases.

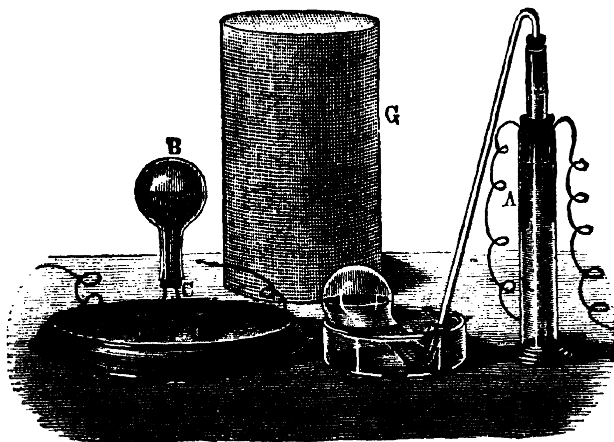
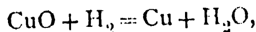


Fig. 50.

Gravimetric Synthesis of Water.—Knowing the composition of water by volume, and also the densities of the two gases, it is easy to calculate the composition of water by weight, but it is important to be able to verify the result by actual experiment.

The method which was first proposed and carried out by Berzelius and Dulong in 1820 consists in passing pure hydrogen over a weighed quantity of red-hot copper oxide, CuO,

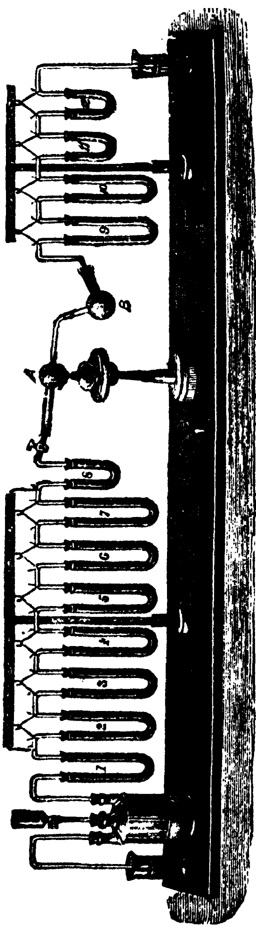


$$CuO + H_2 = Cu + H_2O,$$

wher[illegible]de is *reduced* or robbed of its oxygen, which goes to form w[illegible] with the hydrogen, and leaves metallic copper behind.

By weighing the copper oxide before the experiment and the copper remaining after the experiment, the weight of oxygen used is found. Then by carefully collecting and weighing the water produced, and subtracting the oxygen previously found, the weight of hydrogen used is obtained. The above experimenters found as a mean of four experiments that water was composed of—

	Found.	Calculated.
Oxygen	88.901	88.864
Hydrogen	11.099	11.136
	100.000	100.000



In 1843 Dumas and Stas made a most careful repetition of these experiments, taking every conceivable precaution against experimental errors. The hydrogen which they obtained from sulphuric acid and zinc was passed through a series of U tubes shown in Fig. 51, containing nitrate of lead, sulphate of silver, caustic potash, and phosphorus pentoxide, which serve to purify the gas from traces of sulphuretted hydrogen, arseniuretted hydrogen, sulphur dioxide, oxides of nitrogen, and moisture. The pure hydrogen thus obtained was passed over the weighed bulb A (Fig. 51) containing copper oxide and joined to the bulb B which is also weighed and serves for the collection of the water produced, any water vapour being absorbed by the following weighed U tubes. They found by means of nineteen separate experiments that 840.161 grams of oxygen we[illegible]onsumed in the production of 945 439 grams of water, or [illegible]ercentage composition of water by weight is

Oxygen	88.864
Hydrogen	11.136
	100.000

which agrees exactly with the composition calculated from the volumetric analysis.

Lavoisier's Experiments.—At the end of last century Lavoisier examined the composition of water by the following method, depending on the fact that when water vapour is passed over red-hot iron the oxygen is absorbed, and the hydrogen passes on in the free state.

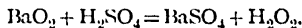


$$3Fe + 4H_2O = Fe_3O_4 + 4H_2.$$

The apparatus used by Lavoisier is of great historical interest. The water was allowed to drop slowly into a tube from which it flowed into a gun barrel, heated in a furnace. Here the decomposition took place, and the hydrogen passed on and was collected and measured in a large bell-jar, whilst any undecomposed steam was condensed, and the water collected and weighed. The results thus obtained are influenced by so many experimental errors that no very exact numbers were obtained, but still the results were sufficiently near the truth for the state of the science more than one hundred years ago.

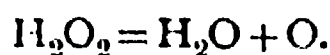
Hydrogen dioxide (or peroxide), H_2O_2

Preparation.—Hydrogen dioxide is an unstable compound only known in solution, and has not been prepared in the pure state; it is obtained by the action of dilute sulphuric acid on barium dioxide,



$$BaO_2 + H_2SO_4 = BaSO_4 + H_2O_2.$$

Properties.—Hydrogen dioxide is so unstable a compound that it is easily decomposed into oxygen and water on slightly raising its temperature,

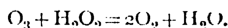


$$H_2O_2 = H_2O + O.$$

It possesses bleaching properties like chlorine, although acting more slowly, and is sometimes used for bleaching hair and old engravings. It acts as a p[illegible]rful oxidising agent, converting ferrous salts into ferric salts i[illegible] an acid, and oxidising black lead sulphide, PbS, to white lead sulpha[illegible]SO_4.

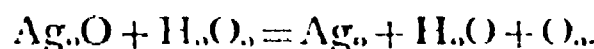
Hydrogen [illegible]tains an atom of oxygen very loosely combined,

and this often abstracts another atom of oxygen, which is also loosely combined, from many other compounds, thus giving rise to the more stable *molecule* of free oxygen. It thus apparently acts as a reducing agent, that is, it abstracts oxygen from other compounds. Thus ozone is decomposed into ordinary oxygen,



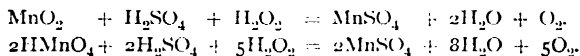
$$O_3 + H_2O_2 = 2O_2 + H_2O.$$

Silver oxide is *reduced* to the metallic state whilst oxygen is set free.



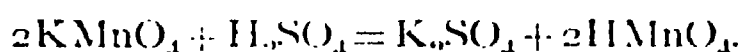
$$Ag_2O + H_2O_2 = Ag_2 + H_2O + O_2.$$

It also *reduces* manganese dioxide and potassium permanganate in presence of sulphuric acid, manganous sulphate being formed and oxygen liberated,



$$MnO_2 + H_2SO_4 + H_2O_2 = MnSO_4 + 2H_2O + O_2.$$
$$2HMnO_4 + 2H_2SO_4 + 5H_2O_2 = 2MnSO_4 + 8H_2O + 5O_2.$$

The potassium permanganate, $KMnO_4$, may be supposed to be decomposed by the sulphuric acid, H_2SO_4, and the free permanganic acid, $HMnO_4$, liberated,



$$2KMnO_4 + H_2SO_4 = K_2SO_4 + 2HMnO_4.$$

This is then reduced to manganous sulphate by the hydrogen peroxide and sulphuric acid, in accordance with the above equation.

What we have learnt

In our twelfth Lesson we have studied the various experimental methods by which the composition of water has been ascertained. We have seen that Cavendish made the first synthesis of water; he showed that two volumes of hydrogen and one volume of oxygen unite together to form water, and nothing else but water. The more exact eudiometric method is described in detail. We have learnt also that when two volumes of hydrogen and one volume of oxygen are combined at a temperature of 132°, two volumes of steam are produced. The electrolytic analysis of water and the explosive properties of electrolytic gas are next described. We have seen how the volumetric methods are confirmed by gravimetric experiments, in which water is produced synthetically by passing pure hydrogen over heated copper oxide. The water produced is weighed, and the weight of oxygen it contains is found by noting the loss in weight of the copper oxide. The weight of hydrogen is then obtained by difference.

The preparation and principal properties of hydrogen dioxide have been described; it is shown that this compound acts as a strong oxidising agent, and yet in many reactions it apparently acts [illegible] a *reducing* agent, owing to its containing an atom of oxygen loosely co[illegible] is unites with another loosely combined atom of oxygen [illegible] a stable molecule of free oxygen.

EXERCISES ON LESSON XII

1. How did Cavendish prove the composition of water?

2. Describe *in detail* the method of making a eudiometric synthesis of water.

3. What is the volumetric composition of steam, and how is it experimentally determined?

4. By what experimental method has the gravimetric composition of water been determined?

5. The density of oxygen being 15.9, calculate the gravimetric composition of water from its volumetric composition.

6. In an experiment on the gravimetric composition of water 0.5278 grams of water were obtained. What weight of copper oxide had been decomposed, and what volume of hydrogen at 15° and 746 mm. had been used to decompose it?

7. How is hydrogen dioxide prepared? Explain its reducing action on Ag_2O, O_3, $KMnO_4$, and MnO_2.

8. What weight of oxygen is contained in 500 c.c. of water measured at 4°?

9. Five grams of water are decomposed by electrolysis. What volume of electrolytic gas measured at 15° and 745 mm. pressure has been obtained?

10. What volume of liquid water is produced by the explosion of 100 c.c. of electrolytic gas (at NTP) in a eudiometer? (1 c.c. of water weighs a gram.)

11. In an experiment on the gravimetric synthesis of water, 150 grams of zinc were dissolved in dilute acid, and the hydrogen passed over heated copper oxide: what weight of copper oxide would be decomposed, and how much water formed?

LESSON XIII

HEAT RELATIONS OF WATER

EXPANSION AND CONTRACTION—POINT OF MAXIMUM DENSITY—TENSION OF VAPOUR—EVAPORATION—MELTING AND BOILING POINTS—LATENT HEAT—FREEZING MACHINES—SPECIFIC HEAT—DULONG AND PETIT'S LAW.

Expansion and Contraction of Water. Point of Maximum Density.—If we cool water from 100° to 0°, it is found to contract until the temperature 4° is reached (or more exactly 3.945), if it is cooled below this point *it expands in passing from* 4° *to* 0°, whilst when the water at 0° becomes ice at 0° (when it freezes), a sudden and great expansion takes place.

It is evident, since water contracts until it reaches 4°, and further cooling causes an expansion, that 4° is the point at which water is denser than at any other, *i.e.* it is the point of maximum density, and is heavier bulk for bulk at this temperature than at any other.

Dr. Hope's Experiment.—This is well shown by an experiment first made by Dr. Hope, which is here slightly modified. Fig. 52 shows a cylindrical vessel, perforated laterally by two holes, in which thermometers are fixed, one at the top and the other at the bottom. Round the centre of the vessel is a shelf containing broken ice. When the vessel [illegible] filled with water at the ordinary temperature of the air, [illegible] 15°, it is noticed that the lower thermometer falls [illegible] 4°, at which

point it remains stationary, whilst the upper one is scarcely affected. This is because the water cools, and contracts, and becomes heavier, and therefore sinks to the bottom. This goes on until the lower half of the water reaches 4°, when no further circulation in that portion takes place. The upper half is scarcely affected, because water is a very bad conductor of heat, but the middle portion of water is soon cooled below 4°, and becomes lighter, and therefore ascends and sets up a circulation in the upper half of the water causing the upper thermometer to begin to fall. It soon indicates a temperature of 0°, whilst the lower one remains stationary at 4°, showing that the water at that temperature is heaviest, sinking to the bottom, and that the water at 0° is lighter, because it rises to the top.

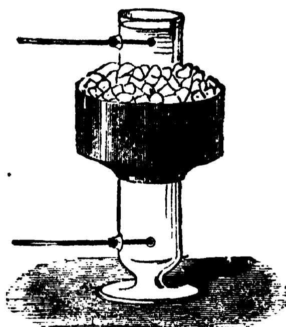


Fig. 52.

Increase in Volume on Solidification.—When water at 0° freezes and becomes ice at 0°, the change of state is accompanied by a sudden and great expansion amounting to about 10 per cent: thus 1 vol. of water at 0° becomes 1.102 vols. of ice at 0°, or an increase in volume of 10.2 per cent. The following table shows the density or specific gravity of ice as compared with water at 0° – 25° C. (water at 4° = 1).

Temperature.	Density.	Temperature.	Density
Ice 0°	0.91674	Water 8°	0.99987
Water 0°	0.99987	,, 10°	0.99973
,, 2°	0.99996	,, 15°	0.99912
,, 4°	1.00000	,, 20°	0.99821
,, 6°	0.99997	,, 25°	0.99708

Effects in Nature.—The force with which water expands on freezing is almost irresistible. This is evidenced by the bursting of strong iron water-pipes in winter. It is popularly believed th[illegible] the *thaw* bursts the pipes, but this is an erroneous conclusi[illegible]m the fact that the pipes first begin to leak when the thaw tak[illegible]ce. It is evident that at the time of bursting

the pipes are filled with solid ice and none can therefore escape. It is only when the ice melts during the subsequent thaw that any leakage of water is seen.

If we examine the effects of the point of maximum density of water being 4°, we see that it is owing to this fact as well as to the expansion on solidification that ice always forms *on the surface* of ponds and lakes. This is a most beneficent provision of nature, for were it not so, our lakes and rivers would, in winter, freeze at the bottom first, and would soon become a solid mass of ice which even all the warmth of summer would probably be unable to thaw. As it is, the whole mass of water in a lake must first reach 4° before the surface layers can freeze; hence very deep lakes seldom freeze. The covering of ice protects the deeper water from the excessive cold, and fish and other aquatic life is preserved through the severest winter, the lowest depths never falling below 4° C.

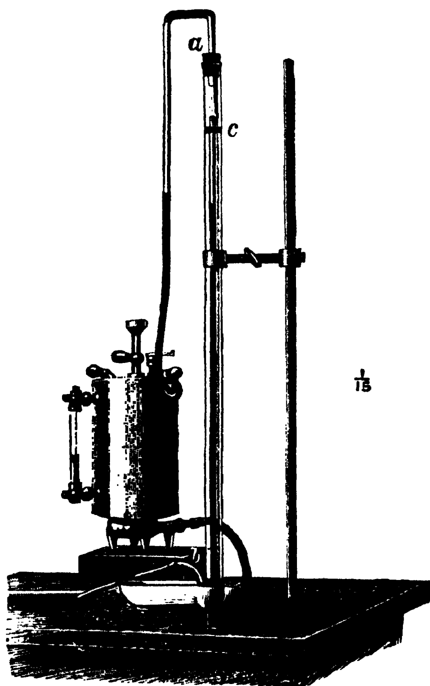


Fig. 53.

The effects of frost in the disintegration of the soil and rocks can now be easily understood. The gravel path which is saturated with water before a frost, is lifted bodily, because all the interstices filled with water are made larger when the water is turned into ice. Hence a thaw leave[illegible] the path in a soft and pulpy condition, because the ice melts [illegible] sinks [illegible] the ground, leaving the gravel slightly un[illegible]ed and very

porous. Rain water, freezing in a crevice in the rocky cliffs of our coasts, exerts an enormous force, rending the rocks and making the gap wider; this action, in time, is sufficient to detach large masses of rock, which are thus hurled down below.

Tension of Aqueous Vapour. Evaporation.—Water, even at the ordinary temperature of the air, is constantly giving off vapour, and we know that if a saucer full of water is left in the open air for a few days it gradually evaporates into the atmosphere. This vapour, which comes off from water (and even from solid ice) at all temperatures, exerts a pressure if it is confined; and this pressure is constant for each temperature. This is known as the elastic force or tension of aqueous vapour, and may easily be seen by taking two exactly similar barometer tubes, and into the Torricellian vacuum of one of them introducing a few drops of water. The mercury in this one will be depressed, the amount of the depression being the greater the higher the temperature. The following numbers show the depression in millimetres of mercury, for water vapour at different temperatures:—

Tension of Aqueous Vapour

Temperature.	Tension.	Temperature.	Tension
Ice at − 10° C.	2.09	40°	54.90
,, 0°	4.60	60°	148.79
Water at + 10°	9.16	80°	354.28
,, 20°	17.39	100°	760.00
,, 30°	31.55	101°	787.63

The above facts explain the more rapid evaporation of water in summer; another factor, however, being the dryness of the atmosphere. Evidently then, when water is heated, the tension of its vapour increases, until at 100° its tension is equal to the atmospheric pressure; and if water is heated to 100° in a Torricellian vacuum, when the atmospheric pressure is 760 mm., the mercury is depressed to the level of that in the trough. The apparatus for showing this will be readily understoo[illegible] rom Fig. 53.

The [illegible] r tensions of other liquids are different from those of water at [illegible] ame temperature, *e.g.* at 0° C. they are—

Vapour Tensions at 0°

Water	4.6 mm.
Alcohol	13 mm.
Carbon bi-sulphide . . .	132 mm.
Ether	182 mm.
Sulphur dioxide (liquid) . .	1165 mm. (boils below 0°)

The vapour tensions of water, alcohol, and ether are clearly shown in Fig. 54. The first is a barometer tube with a Torricellian vacuum; into the other three have been introduced 1st, water; 2nd, alcohol; 3rd, ether, so as to saturate the space with their vapour, and produce the maximum tension for that temperature.

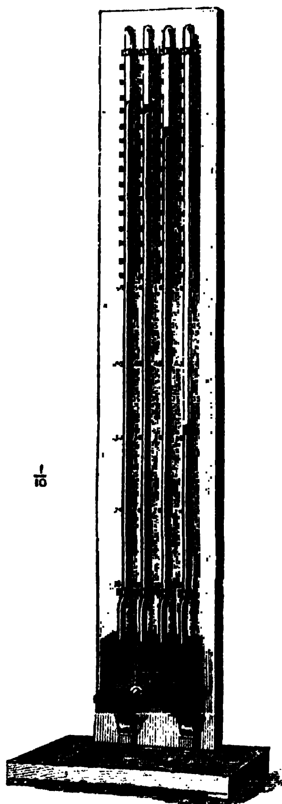


Fig. 54.

Expt. 45. **Melting and Boiling Points of Water. Latent Heat.**—If we fill a beaker with pounded ice and apply heat by a Bunsen burner, we notice that the thermometer placed in it indicates 0° C., and although heat is constantly being given to the ice, *no increase of temperature takes place* until the ice is melted; the only effect of the heat is to melt the ice or change its state from solid to liquid. This heat which is absorbed without raising the temperature is called "the latent heat of fusion." When all the ice is melted, the temperature of the water rises until 100° is reached, at which point the water boils. When this point is reached *no further increase of temperature takes place*, any additional heat merely causing a chang[illegible] from liquid to gaseous water. He[illegible]ain the heat required to vaporise water is rendered latent. [illegible] is called the "latent heat of vaporisation."

Influence of Pressure on the Melting and Boiling Points.—We shall see that a liquid boils when the tension or pressure of its vapour is equal to the pressure above it, hence it is only correct to say that water boils at 100° C., when the atmospheric pressure is at its normal, viz. 760 mm. Under diminished pressure water boils at a lower temperature, and under increased pressure water boils at a higher temperature than 100°. Hence it is important, in graduating a thermometer, to read off the exact pressure at which the boiling point is marked on the stem. On Mont Blanc water boils at 85°, and eggs cannot there be cooked by boiling in an open vessel; whilst under a pressure of two atmospheres water does not boil until 120.6° is reached, and at twenty atmospheres' pressure water boils at 213°. Knowing the temperatures at which water boils under different pressures, it is possible to measure the heights of mountains by means of the thermometer. It is only necessary to determine the temperature at which water boils at the summit and at the base or the sea-level. From these determinations the atmospheric pressure can be deduced, and from this the height of the place at which the experiment was made.

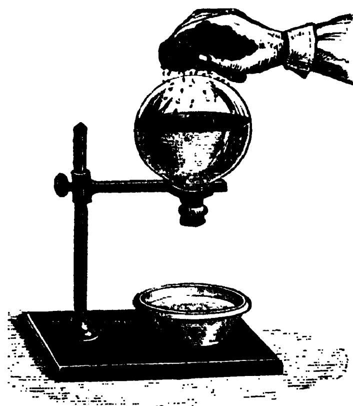


Fig. 55.

EXPT. 46.—A simple experiment will show that, under diminished pressure, water boils at a lower temperature; and, paradoxical as it may seem, it is possible to boil hot water by cooling it. Fig. 55 shows the method of doing this. Water is boiled rapidly in a strong round-bottomed glass flask, furnished with a stopper, through which an ordinary gas tap is passed; whilst the water is boiling, the tap is closed, the heat at the same moment being withdrawn. The flask is now inverted in a retort-stand ring, and a shower of cold water poured over it from a sponge. The water immediately begins to boil afresh,

because the steam in the upper part of the flask is thus condensed, and the pressure on the hot water released. Under these conditions the water is still hot enough to boil under the diminished pressure.

In the same way the melting point of ice is influenced by pressure, but to a much smaller extent; under increased pressure the melting point of ice (and of all substances which expand on solidifying) is *lowered*. Under a pressure of 16.8 atmospheres ice melts at – 0.126° C.

On the other hand, bodies which contract on solidification, such as sulphur, wax, etc., exhibit an opposite change, for the melting point is *raised*.

Definition of Boiling Point.—We may now define the boiling point of water (or of any other liquid) as *that point at which the tension of its vapour is equal to the superincumbent atmospheric pressure*, and it is clear that water boils exactly at 100° only when the atmospheric pressure is 760 mm.

Latent Heat of Fusion. How it is Measured.—When steam condenses to liquid water, its latent heat is given off as sensible heat. Similarly, when water freezes to solid ice, its latent heat of fusion is given off as sensible heat, and in these operations just as much heat is given out as is required to perform the opposite change of water into steam, or ice into water.

EXPT. 47. **Ice on melting Absorbs Heat.**—If we take a kilogram of water at 80° and mix it with a kilo of liquid water at 0°, the result is 2 kilos of water of 40°, or 1 kilo in falling from 80° to 40° has lost just as much heat as is required to raise it from 0° to 40°. But if we mix a kilo of water at 80° (more exactly 79.25°) with a kilo of ice at 0°, the result is 2 kilos of water at 0°. In other words, the hot water has given out just sufficient heat to *melt* the ice, but none in addition to raise the temperature of the liquid water. Or ice, in melting, requires as much heat as would raise its own weight of water through 80°, or 80 times its weight through 1°.

The Thermal Unit or Calorie.—Hence the latent heat of fusion of water is 79.25 thermal units; a *thermal unit* being the amount of heat required to raise a kilogram of *water* from 0° to 1° C.; this is called a *Calorie*.

[In France the thermal unit is that quantity of heat which is necessary to raise 1 *kilogram* of water from 0° to 1° C., and is called the *Calorie*. In England the thermal unit is that amount of heat which will raise 1 *pound* of water from 0° to 1° C., and is called the pound-degree unit.

[1 thermal unit (English) = 0.45 Calorie.]

EXPT. 48. **Water on Freezing gives out Heat.**—That the latent heat of fusion is given off by water, when it passes from the liquid state at 0° to the solid state at 0°, may be shown by placing a metal vessel containing cold water in a bath of mercury, at a temperature say of – 15.° * By placing a thermometer in the mercury bath, and also in the water, it will be found that whilst the temperature of the water falls to 0°, that of the mercury rises; but whereas, during the passage of the liquid water into solid ice, the thermometer placed in it shows no alteration, but remains constant at 0°, that in the mercury *continues to rise rapidly*, indicating that the latent heat is being given out by the water as sensible heat.

Latent Heat of Steam.—The latent heat of steam is given out as sensible heat when steam condenses to water, and this affords a means of ascertaining its amount.

EXPT. 49.—If we pass steam at 100° into a kilogram of water at 0° until the water is raised to 100°, it will be found that the weight of water is now 1.187 kilos, or 0.187 kilo of steam at 100° has given out sufficient latent heat in condensing to raise 1 kilo of ice-cold water through 100°, or 1 kilo of steam would raise 5.36 kilos of water from 0° to 100°, or 536 kilos through 1°. Hence the latent heat of steam is said to be 536 thermal units or Calories.

The apparatus for showing this experiment will be readily understood from Fig. 56.

Water Frozen by its own Evaporation.—We have already seen that when liquid water (or any other liquid) passes into the gaseous state, a large amount of heat is absorbed, or becomes latent, in order to keep it in that state. Not only is this true of water when it is boiled by the application of heat, but it is also true of water which slowly evaporates.

* Temperatures below the freezing point are indicated by a minus sign placed before the figures.

Expt. 50.—A beautiful experiment will illustrate this. Fig. 57 shows Wollaston's Cryophorus, which consists of two glass bulbs connected by a glass tube. Water is placed in B, and this is briskly boiled until the steam has driven out all the air in both bulbs through the open tube at the lower end of A; this is then sealed up by the blowpipe, the lamp which boils the water being at the same instant withdrawn. After the apparatus has cooled, all the water is allowed to run into B, whilst A is placed in a freezing mixture. The tension of aqueous vapour is now much reduced in A, when aqueous vapour passes over from B to A so rapidly (tending to produce an equilibrium of pressure), and so much heat is absorbed from the water by the vapour passing over, that the

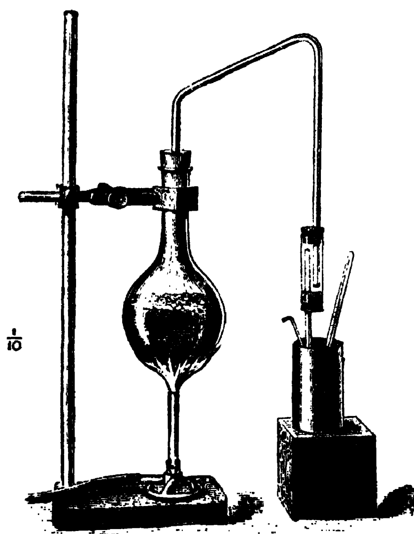
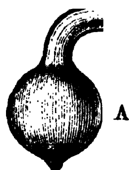


Fig. 56.



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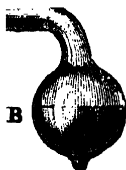


Fig. 57.

remaining water is cooled down below 0°, and freezes to a solid mass of ice.

Carré's Freezing Machine.—This principle has been applied on a practical scale for the production of [illegible] Fig. 58 shows an apparatus which is known as Ca[illegible] Freezing Machine.

Water in the strong bottle C is in communication with a reservoir B, containing strong sulphuric acid, which has the power of absorbing water vapour rapidly. The reservoir can be exhausted of air by the air-pump A. After working the pump for a few minutes, the pressure in C is so much reduced that the water begins to boil, and so much heat is rendered latent in the vapour which passes over into B, that the water in C is soon cooled below 0°, and freezes to a solid mass of ice. The tap is now closed, and the bottle removed.

Freezing Mixtures.—In many cases, when salts are mixed with water, their solution is accompanied by a diminution of temperature owing to the absorption of sensible heat which becomes latent during the passage of the salt from the solid to the liquid state, *e.g.* when 500 grams of potassium sulpho-cyanide, KSCN, is mixed with 400 grams of cold water, the temperature sinks to −20°. When 32 parts of common salt, NaCl, are mixed with 100 parts of pounded ice or snow, the two solid bodies become liquid, and so much heat is rendered latent that the temperature sinks to −23°. Equal weights of crystallised calcium chloride, $CaCl_2 . 2H_2O$, and snow, when mixed together, give a freezing mixture, the temperature of which sinks from 0° to −45° C.

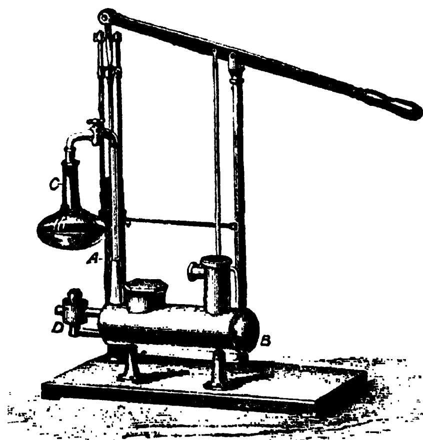


Fig. 58.

In the case, however, of mixing many anhydrous salts with water a chemical combination takes place in which heat is evolved ... anhydrous calcium chloride, $CaCl_2$, becomes hot when mixed with water, because this salt has such a great chemical attraction for water.

Specific Heat.—We have seen that the thermal unit is that amount of heat which will raise a kilo of water through 1°, and has reference to water only. A unit weight of iron or copper would require a *different* amount of heat to raise its temperature 1°. Different bodies have different capacities for absorbing heat, and they give out different amounts of heat on cooling through the same interval of temperature. This is expressed by saying that they have different *specific heats* (*or calorific capacities*). *The specific heat of a substance is the ratio between the amount of heat required to raise its temperature through a certain interval, compared with the amount of heat required to raise the same weight of water through the same interval. It is expressed by the number of thermal units required to raise a unit weight of the substance through 1° of temperature, e.g.* only $\frac{1}{30}$ as much heat is required to raise 1 gram of mercury 1° as is required to raise 1 gram of water 1°; hence, we say, the specific heat of mercury is $\frac{1}{30}$ or .33. The specific heat of water is taken as the standard with which all others are compared, *e.g.*—

Specific Heats

Water	1.0000	Lead	0.0314
Copper	0.0939	Mercury	0.0332
Bromine	0.0843	Iodine	0.0541
Arsenic	0.0822	Sodium	0.2930

Dulong and Petit's Law.—It was found by Dulong and Petit that the product of the specific heat into the atomic weight of solid elements is approximately constant, being about 6.3. Hence the specific heat of an element is sometimes of value as a control in determinations of atomic weight. The following will serve as examples:—

	Specific Heat (of Equal Weights).		Atomic Weight.		Atomic Heat (of Atomic Weights).
Antimony .	0.0513	×	119.4	=	6.12
Bismuth .	0.0308	×	206.4	=	6.35
Cadmium .	0.0567	×	111.3	=	6.31
Gold . .	0.0324	×	195.7	=	6.34
Iron . .	0.1138	×	55.6	=	6.32
Zinc . .	0.0956	×	65.0	=	6.21

In other words, if instead of taking *equal weights* of these elements for the determination of their specific heats, we take *atomic weights*, then we find that the specific heat (of the atom) is constant, or *the same amount of heat is n[illegible]d to heat an atom* (*or an equal number of atoms*) *of any of [illegible] solid elements to the same extent.*

It is evident from the above that *the specific heats of the solid elements are inversely proportional to their atomic weights*, or,

$$\text{Specific heat} = \frac{1}{\text{Atomic weight}} \times 6.3$$

approximately, and therefore we find that the

$$\text{Atomic weight} = \frac{6.3}{\text{Specific heat.}}$$

From this last equation it is easily seen how the determination of specific heat may be, and has been, used as a control in the determination of the atomic weights.

Specific Gravity or Relative Density

Not only is water taken as the standard substance by which to compare specific heats and to define thermal units, but, just as hydrogen is taken as the standard with which to compare the densities of all gases, so water is taken as the standard with which to compare the densities or *specific gravities* of all liquid and solid bodies. When we say that the *specific gravity* or relative density of cast iron is 7.5, we mean that, volume for volume, the metal is seven and a half times as heavy as water, or a piece of cast iron whose volume is a cubic centimetre weighs 7.5 grams, for we learnt on p. 39 that a cubic centimetre of distilled water at 4° weighed 1 gram. When we say that the specific gravity of ether $(C_2H_5)_2O$ is 0.72, we mean that it is only about three-quarter times as heavy as water. The metal sodium is lighter than water, its specific gravity being 0.974, whilst that of pine wood is 0.5.



Fig. 59.

Use of Specific Gravity Bottle.—When we want to find the specific gravity of a liquid, the simplest method is to compare the weights of exactly equal volumes of that liquid and water. For this purpose the specific gravity bottle is used (Fig. 59); these are generally adjusted to hold exactly 50

grams of distilled water when filled at 60° F., the mean temperature of the air. Then all that is necessary is to weigh the clean and dry specific gravity bottle filled with the liquid to be examined, taking care that it has a temperature of 60°, and is completely filled, so that when the perforated stopper is inserted, the excess of liquid emerges from the hole in the stopper, and is then carefully removed.

Specific Gravity of Solid Bodies.—There are many methods of finding the specific gravity of solid bodies, but nearly all depend upon the principle of Archimedes, viz. that when a solid body is *weighed whilst fully immersed in water, it loses weight equal to the weight of an equal volume of water.* For the proof of the accuracy of this principle, as well as for further details about the methods of finding specific gravities, a book on Physics must be consulted.

The specific gravity of brass borings, for example, may be found by first weighing them in air and then putting them in the specific gravity bottle, filling up with water and again weighing.

The second weighing will evidently be: weight of brass + weight of bottle + weight of water required to fill empty bottle (= 50 grams) *minus* weight of water *displaced* by the brass. From this we get the weight of an equal bulk of water. In all cases the specific gravity is then calculated by dividing the weight of the substance by *the weight of an equal bulk of water*, or

$$\text{Specific gravity} = \frac{\text{Weight of known volume}}{\text{Weight of equal vol. of water.}}$$

What we have learnt

In our thirteenth Lesson we have seen that water expands when it is heated, and contracts when it is cooled, but that there is a limit to its contraction, viz. at 4°, below which temperature further cooling causes it to expand until 0° is reached, when a further sudden expansion takes place, amounting to about ten per cent of its volume, the water at 0° freezing to ice at 0°. Water-pipes are burst by this sudden expansion on freezing, and not by the subsequent thaw as is often supposed.

If we apply heat to ice at, say −10°, its temperature is not raised above 0°, at which point the application of more heat merely causes it to change from the solid to the liquid state. When all the ice is melte[illegible] further heat raises its temperature until 100° is reached, when the w[illegible]; further application of heat cannot raise its temperature above 100°, it merely causes the water to change its state from a liquid to a gas.

Thus in heating ice from $-10°$ to $100°$, we have two stationary points as regards temperature, viz. $0°$ and $100°$, called the freezing point (or melting point) and boiling point. The boiling point of water is greatly influenced by pressure: water boils at a lower temperature under diminished pressure and at a higher temperature under increased pressure. The heat absorbed by a body changing its state from solid to liquid or liquid to gas is called latent heat, and is again given out when the body changes its state in the opposite direction, viz. from gas to liquid or liquid to solid. We have seen how to measure the amount of the latent heat of steam and the latent heat of fusion of ice, and considered the part played by latent heat in freezing machines and freezing mixtures. We have defined specific heat, and considered Dulong and Petit's Law, that the product of the specific heat into the atomic weight of the solid elements is approximately constant. We have seen that water is taken as the standard with which all liquid and solid bodies are compared as regards their density or specific gravity; and we have seen the relation between specific gravity and weight in the metric system, and also learnt how specific gravity is found by experiment.

Exercises on Lesson XIII

1. Describe the behaviour of water which is (*a*) cooled from $100°$ to $-10°$; (*b*) heated from $-10°$ to $100°$, mentioning all the important facts observed.

2. What is the influence of pressure on the melting and boiling points of water?

3. What is meant by latent heat? How may it be measured?

4. Define specific heat and explain Dulong and Petit's Law.

5. Describe experiments showing how water may be frozen by its own evaporation.

6. Explain the principle of freezing mixtures.

7. Define a thermal unit.

8. Define specific gravity. An empty specific gravity bottle weighs 15.4268 grams; filled with water at 60° F. it weighs 66.0694 grams; when filled with a sample of sulphuric acid it weighs 106.2378 grams. What is the density of the acid?

9. The above bottle weighed 73.4586 grams when 8.4204 grams of brass turnings had been placed in it and the bottle filled up with distilled water. What is the density of the brass?

10. A piece of glass rod weighed in air 4.2882 grams, it weighed in water 2.4787 grams. What is its density?

11. What weight of ether of specific gravity 0.7204 will the bottle hold which is mentioned in No. 8?

12. What is the weight of an iron casting—its volume is 476 c.c. and its density 7.436?

13. An iron bottle has a capacity of 784 c.c. What weight of mercury can it hold, the density of mercury being 13.59?

LESSON XIV

WATER AS A SOLVENT—WATER OF CRYSTALLISATION EFFLORESCENCE, DELIQUESCENCE—SOLUBILITY OF GASES—NATURAL WATERS—TEMPORARY AND PERMANENT HARDNESS AND THE SOFTENING OF WATER—DISTILLATION AND PURIFICATION.

Water as a Solvent.—Water is the most generally useful of all the known solvents; nearly all the re-agents of the Chemical Laboratory are used in aqueous solution. Not only do very many solid substances, especially metallic salts, dissolve in water, but certain liquid compounds, *e.g.* alcohol and acetic acid, as well as nearly all gases, dissolve in water to a greater or less extent.

Solubility of Salts.—The weight of solid compounds which can be dissolved in a given weight of water depends not only on the nature of the compound, but also on the temperature at which solution is effected. The maximum amount of each substance which water is capable of dissolving at a given temperature is fixed and definite, and when water has taken up this amount it is said to be a *saturated* solution of the substance dissolved.

EXPT. 51.—In order to show the different solubilities of salts let us take 30 grams of powdered potassium chlorate and place it in a flask with 100 c.c. of water at 30° C. Let us now shake the flask until the water becomes saturated; we see that all the salt has not dissolved. Let us now filter the solution through filter paper placed in a funnel and evaporate the liquid to dryness over a small flame. We see that a white

residue is left, which may be collected and heated in a test tube to prove that it is potassium chlorate. We see that although *all* this salt has not been dissolved by cold water, yet a portion of it has been dissolved.

EXPT. 52.—Let us now repeat the experiment, but instead of shaking up in the cold we will boil the salt with the water; this time it all dissolves, showing the influence of temperature on the amount of a salt which can be dissolved. We notice that on cooling the solution a portion of the potassium chlorate is deposited as crystals.

EXPT. 53.—Repeat the Experiment 51, but use cold water and magnesium sulphate instead of potassium chlorate, but in the same quantities. We notice that all this salt dissolves even in the cold.

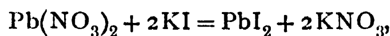
EXPT. 54.—If we repeat the Experiment 51 with barium sulphate we find that the filtered solution gives no residue on evaporation, showing that the compound is quite insoluble; and it is so even in boiling water.

The above facts are well indicated in Fig. 60, which represents graphically the effect of (1) the nature of the compound, and (2) the temperature at which solution is effected. The vertical lines indicate temperatures from 0° to 100° C., whilst the horizontal lines indicate the number of grams of the salt which can be dissolved by 100 grams of water at each particular temperature, *e.g.* we notice on the curves of solubility for potassium nitrate and lead nitrate that at 50° both salts are equally soluble, 100 grams of water dissolving 85 grams of either compound. The two curves also show that the potassium salt is less soluble at low temperatures and more soluble at higher temperatures than is lead nitrate.

Very many salts dissolve but very slightly in water, especially cold water, *e.g.* lead chloride, $PbCl_2$, calcium sulphate, $CaSO_4$, strontium sulphate, $SrSO_4$ (very sparingly soluble), silver nitrite, $AgNO_2$, silver sulphate, Ag_2SO_4, lead iodide, PbI_2; whilst others are practically insoluble in water, such as barium sulphate, $BaSO_4$, silver chloride, AgCl, lead chromate, $PbCrO_4$.

Precipitation.—Whenever the solutions of two salts are mixed together, and by a double decomposition a difficultly soluble or insoluble salt can be produced, then that compound

separates from the solution in the solid state, and is said to be *precipitated*. Thus



$$Pb(NO_3)_2 + 2KI = PbI_2 + 2KNO_3,$$



$$AgNO_3 + NaCl = AgCl + NaNO_3.$$

Crystallisation.—When any salt is dissolved in water, say boiling water, there is a certain limit to the quantity of

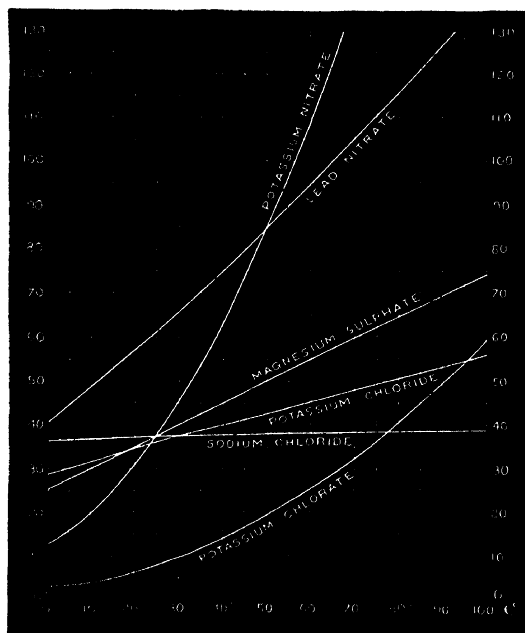


Fig. 60.

salt above which no more salt can be dissolved. The solution is, as has been stated, then said to be saturated. If now the solution be cooled, the water is usually no longer able to hold all the salt in solution, and a portion of it separates out in the solid form, and generally in the form of crystals of definite shape. Thus from Fig. 60 we may learn that at 100° a saturated solution of potassium chlorate contains 60 parts of

the salt per 100 of water, whilst at 15° (the ordinary temperature of the air) only 5 parts of the salt can be dissolved. Evidently, then, a saturated solution at 100° must deposit 55 parts of the salt as crystals on being cooled down to 15°. Similarly a saturated solution of nitre (potassium nitrate) at 70° if cooled to 15° must deposit just twice as much, or 110 parts, of the salt as crystals.

Water of Crystallisation.—Very often when metallic salts crystallise from aqueous solution they do so as definite chemical compounds with water. This water, which is in the solid state and in combination with the salt (doubtless combined with it in the solution also, before crystallisation), is called Water of Crystallisation, *e.g.*

Sodium sulphate or Glauber's salts . .	$Na_2SO_4 . 10H_2O$
Sodium carbonate or washing soda . .	$Na_2CO_3 . 10H_2O$
Sodium borate or borax	$Na_2B_4O_7 . 10H_2O$
Calcium sulphate or gypsum . . .	$CaSO_4 . 2H_2O$
Copper sulphate or blue vitriol . . .	$CuSO_4 . 5H_2O$
Ferrous sulphate or green vitriol . . .	$FeSO_4 . 7H_2O$
Zinc sulphate or white vitriol . . .	$ZnSO_4 . 7H_2O$
Magnesium sulphate or Epsom salts . .	$MgSO_4 . 7H_2O$
Aluminium potassium sulphate or common alum	$Al_2(SO_4)_3K_2SO_4 . 24H_2O$

Efflorescence.—Many salts containing water of crystallisation are not able to retain it all in a dry atmosphere, and on exposure to the air they become opaque, lose a part of their water, and fall to powder; they are then said to effloresce.

EXPT. 55.—Expose a few crystals of washing soda to a dry warm atmosphere and notice their gradual efflorescence.

Deliquescence.—Other salts, on the other hand, attract water with such great avidity (when they are said to be hygroscopic) that they liquefy if exposed to the air owing to the absorption of moisture, *e.g.* calcium chloride, potassium acetate, and ferric chloride. The first named is used in the anhydrous * state as a drying agent.

EXPT. 56.—Expose some dry calcium chloride to the air in a dish and notice how soon it becomes moist and gradually deliquesces to a liquid.

* Anhydrous means without water.

Solubility of Gases.—All gases dissolve to a greater or less extent in water.

Such gases as hydrogen, oxygen, nitrogen, air, or nitric oxide, dissolve but slightly in water; thus a litre of water will dissolve only 20.92 c.c. of oxygen and nitrogen from the air at 15° C. (see p. 135). Other gases, such as nitrous oxide, chlorine, sulphuretted hydrogen, and carbon dioxide, are more soluble, whereas other gases, such as hydrochloric acid, HCl, ammonia, NH_3, sulphur dioxide, SO_2, are exceedingly soluble in water.

Influence of Temperature.—The effect of temperature on the solubility of gases in water is the opposite to that on the solubility of solids, for the higher the temperature the less gas is dissolved, and boiled water, especially if boiled in a vacuum, contains no dissolved gases; *e.g.* a litre of water dissolves

23.34	c.c. of nitrogen	and oxygen	from air at	10° C.
19.20	,,	,,	,,	20° C.
17.69	,,	,,	,,	25° C.

Influence of Pressure. (Law of Henry).—The volume of gas (measured at a constant pressure) which can be dissolved by water is *proportional to the pressure* at which the solution is effected. Thus a litre of water will absorb 4 times as much carbon dioxide under a pressure of 4 atmospheres as it would under a pressure of 1 atmosphere. This law was expressed by the discoverer (Henry) that "under equal circumstances of temperature, water takes up in all cases *the same volume of condensed gas as of gas under ordinary pressure.*" This is evidently the same as the first statement, for from Boyle's Law we know that the volume of a gas is inversely proportional to the pressure. Therefore 4 volumes at 1 atmosphere become 1 volume at 4 atmospheres, and if 1 volume of gas is dissolved under 1 atmosphere, under 4 atmospheres 1 volume of gas will still be dissolved; but as this *at constant pressure* (1 atmosphere) would be 4 volumes, we may say that the volume dissolved (measured at constant pressure) *is proportional to the pressure.* We can now understand why it is that on opening a bottle of soda-water the liquid begins to effervesce. It is because carbon dioxide has

been dissolved *under pressure*, and has taken up much more than it can hold under the ordinary pressure of the air, hence a portion of it escapes immediately the pressure is relieved by opening the bottle.

EXPT. 57.—Take a soda-water bottle which is closed by an ordinary cork, and pierce the cork with a hollow borer which is connected with a piece of tubing passing under the bee-hive shelf of the pneumatic trough. When the cork is quite pierced a sudden rush of carbonic acid will be noticed, and this can be collected in the gas jar placed over water to receive it.

Use of dissolved Air in Natural Waters.—The dissolved air in water is of great importance in nature. By its means fishes and all aquatic animals are supplied with the oxygen necessary for their life. In water which has been boiled, so as to expel the dissolved air, and then allowed to cool, fishes soon die for want of air. In water analysis also, the determination of the amount of dissolved oxygen is of importance, because if a particular water is very impure, minute living organisms called *bacteria* thrive in it, and these use up the dissolved oxygen; this loss of free oxygen can be detected by analysis, and so an inference drawn as to presence or absence of the organic impurities which favour the growth of the bacteria and the consequent loss of dissolved oxygen. Boiled water which has been allowed to cool in absence of air is insipid and tasteless, whereas a glass of spring water is refreshing, a difference due almost entirely to the presence or absence of dissolved air.

Natural Waters.—We may divide natural waters into (1) Rain Water, (2) Spring Water, (3) River Water, and (4) Sea Water.

Rain Water.—Rain water is the purest form of natural water, and may indeed be called natural *distilled* water, for it is produced by the slow evaporation (or distillation) of the water on the surface of the earth, the vapour of which rising into colder regions of the atmosphere becomes condensed in the form of clouds, which on further cooling fall as rain. Although rain water is free from the soluble impurities derived from the surface of the ground, yet it is not perfectly pure, because, in falling through our atmosphere, it has washed out certain impurities which are found there in larger or smaller

quantities, *e.g.* near large towns the atmosphere contains small quantities of tarry matter, soot, as well as sulphur dioxide and sulphuric acid, both derived from the burning of coal which contains small quantities of iron pyrites (FeS_2), hence such water has an acid reaction. Rain water also dissolves a certain amount of free nitrogen and oxygen as well as carbon dioxide from the air (see p. 135). It contains, in addition, minute quantities of common salt, ammoniacal salts, nitrites and nitrates, and organic matter as well as mineral particles which float in the atmosphere as dust.

Spring Water.—When rain water percolates through the earth it dissolves a certain amount of the materials with which it comes in contact; the quantity and kind of impurity thus taken up depends upon the nature of the soil and strata through which the water passes. Hence when the water emerges at the surface of the earth as a spring at a lower level than that of the gathering ground, it always contains dissolved mineral matter as well as a larger proportion of carbon dioxide derived from the soil.

River Water.—River water differs from spring water in its not having, as a rule, filtered through various depths of porous strata. It is consequently generally turbid, and contains more or less insoluble matter in suspension, whereas spring water is usually clear and sparkling. River water may be greatly purified by filtration through beds of sand or other material, but this process only removes the suspended impurities. The clear filtered water still contains soluble impurities just as spring water does. On a large scale water is sometimes softened by the addition of lime before it is filtered. The composition of the mineral impurities of river water varies considerably with the nature of the ground over which the water runs; thus Thames water contains about 11 grains per gallon of carbonate of lime, the Trent 21 grains of sulphate of lime. They are both hard waters;* the first is temporarily hard, whilst the second is permanently hard. The waters of the Dee and the Don in Aberdeenshire, draining a granitic district, are, on the other hand, soft waters. In addition to its natural ingredients river water is very often polluted with the sewage of towns and the refuse from manufactories and

* For an explanation of hard and soft waters see p. 123.

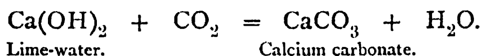
mines, and it is now an important matter to prevent this pollution, and to devise suitable means of purifying such liquids before they flow into the rivers.

Sea Water.—Sea water contains the largest amount of dissolved solids, the mean quantity being about 3.6 per cent, of which common salt (NaCl) makes up 2.6 per cent, the rest being mainly composed of the sulphates, chlorides, and carbonates of magnesia, lime, and potash.

Hard and Soft Waters.—When the mineral matters in solution in natural waters have no action on soap and do not retard the formation of a lather when one washes the hands, such water is said to be soft water. Rain water is of course soft water, because it has had no opportunity of dissolving saline matter, so also is water which has only flowed over granitic rocks or sandstone, which are insoluble in water. But rain water which has come in contact with limestone rocks or chalk (made up mainly of calcium carbonate, $CaCO_3$), or which contains gypsum (calcium sulphate, $CaSO_4$) in solution, decomposes a portion of the soap and so retards the formation of a lather in washing. Hard water renders a portion of the soap useless, because it produces an insoluble compound with the soap. Hardness in water may be of two kinds, either (1) temporary hardness, or (2) permanent hardness.

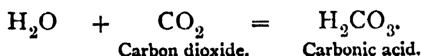
Temporary Hardness.—The presence of dissolved carbon dioxide in water has an important effect as regards its power of dissolving certain mineral substances.

EXPT. 58.—If we take a dilute solution of lime-water and pass a current of carbon dioxide through it, we notice first that a white precipitate of calcium carbonate is formed, for this substance is insoluble in pure water.



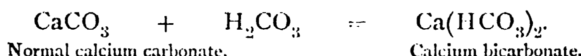
$$\underset{\text{Lime-water.}}{Ca(OH)_2} + CO_2 = \underset{\text{Calcium carbonate.}}{CaCO_3} + H_2O.$$

If, however, we continue to pass the gas through the turbid liquid we notice that it gradually becomes clear, and soon all the precipitate disappears; this is because the water now contains free carbonic acid; thus



$$H_2O + \underset{\text{Carbon dioxide.}}{CO_2} = \underset{\text{Carbonic acid.}}{H_2CO_3}.$$

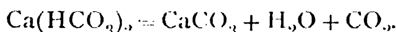
This has the power of dissolving calcium carbonate, the bicarbonate * of calcium being formed ; thus



$$CaCO_3 + H_2CO_3 = Ca(HCO_3)_2.$$

Normal calcium carbonate. Calcium bicarbonate.

Bicarbonate of lime is the principal substance which causes temporary hardness in water, and it may be taken as a type of the rest. This hardness is called temporary because it may be got rid of by boiling, or by precipitation with lime. By this means the bicarbonate is decomposed, the normal carbonate being precipitated, whilst carbonic acid is freed and expelled as CO_2 ; thus

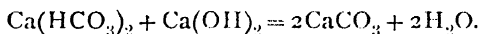


$$Ca(HCO_3)_2 = CaCO_3 + H_2O + CO_2.$$

EXPT. 59.—Boil a portion of the clear liquid obtained by passing CO_2 into lime-water. A white precipitate is again formed, whilst bubbles of CO_2 are given off.

If we shake up equal volumes of the boiled and unboiled water with a measured volume of soap solution added gradually, we shall find that a much larger quantity of soap is required to produce a lather in the case of the unboiled or hard water than is required for the boiled or softened water.

Clark's Process for softening Water.—Temporary hardness due to calcium bicarbonate may be got rid of and the water softened by the addition of a proper proportion of lime, sufficient in quantity to combine with the free carbonic acid and also to decompose the bicarbonate of lime present ; thus



$$Ca(HCO_3)_2 + Ca(OH)_2 = 2CaCO_3 + 2H_2O.$$

The result is that the normal carbonate of lime is produced in a liquid which contains no free carbonic acid to dissolve it, hence it falls as an insoluble precipitate. †

Permanent Hardness.—Hardness which cannot thus be got rid of by boiling is said to be permanent hardness. It is mainly due to gypsum, $CaSO_4$, or to the sulphates or chlorides

* The student should refer to page 205 for an explanation of normal and acid salts.

† Temporary hardness may be due to the presence of the bicarbonates of lime, magnesia, iron, or manganese.

of lime and magnesia which are soluble in water. Boiling has no effect on the solutions of these salts, but they may be decomposed by the addition of common washing soda, sodium carbonate, $Na_2CO_3, 10H_2O$; thus



$$CaSO_4 + Na_2CO_3 = CaCO_3 + Na_2SO_4.$$

Hence the use of washing soda for softening water. The sodium sulphate produced by the double decomposition has no effect on the soap. Water softened by the addition of sodium carbonate is not suited for drinking purposes, inasmuch as it contains sodium sulphate in solution (see equation).

EXPT. 60.—Make a dilute solution of calcium sulphate and divide it into two portions; boil one of them and observe that there is no precipitate as in the former case. Now test both waters with soap as before; both are alike, showing that boiling has had no effect. Soften a third portion of the solution by the addition of a little washing soda, and test again with soap solution. It will be seen that the hardness has disappeared.

Purification of Natural Waters.—Natural waters, especially river waters (*e.g.* the Thames), although not pure enough for domestic or drinking purposes, may be rendered fit for such use by a proper method of purification. We may divide such processes into (1) softening, (2) precipitation or subsidence, (3) filtration.

The method of softening hard waters has already been mentioned, on the large scale; softening by lime is usually employed (Clark's process), and the precipitated carbonate of lime allowed to subside. This subsidence of solid particles or precipitation carries down a large proportion of the suspended matter, the remainder being got rid of by filtration through large filter-beds of sand and gravel. Subsidence and filtration only free the water from suspended matter, whilst the chemical process of softening removes the soluble bicarbonates and sulphates of lime, magnesia, etc. The other soluble impurities cannot be got rid of by these methods.

Distillation of Water.—In order to obtain water free from these soluble impurities it must be distilled.

EXPT. 61.—Place some water coloured blue with copper sulphate in a retort (Fig. 61), and heat it with a Bunsen burner.

When it begins to boil and the steam passes through the glass tube, which is cooled on the outside by a jacket through which a current of cold water flows, it will be seen that the condensed steam is quite colourless water, and that it has been separated from the soluble impurity (copper sulphate), which is left behind in the still.

Volatile Impurities in Water.—In order to obtain pure water, however, simple distillation is not sufficient, as some of the impurities derived from organic matter are volatile, and pass over with the steam into the condenser, and so obtain access to the distilled water.

EXPT. 62.—Repeat Experiment 61 with the addition of a single drop of ammonia instead of copper sulphate. The am-

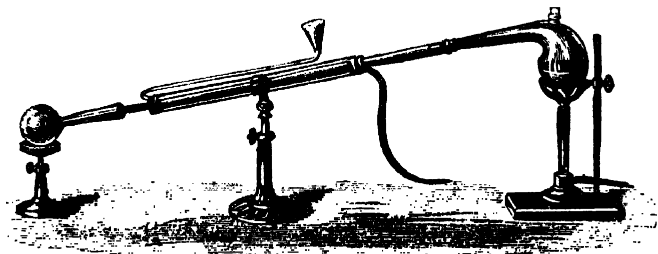


Fig. 61.

monia may be detected in the clear distillate by adding 1 c.c. of Nessler's solution,* when a deep-brown coloration is produced, showing that even the distilled water contains a volatile impurity.

In order to obtain water free from these volatile impurities, the water must first be boiled with a strong solution of potassium permanganate, $KMnO_4$, and caustic potash, KOH. These oxidise and decompose the organic matter, and the volatile products pass over into the condenser with the first portion of steam, the condensed water from which must be rejected as

* Nessler's solution is made by dissolving 62.5 grams of potassium iodide in about 250 c.c. of water, and gradually adding a cold saturated solution of mercuric chloride until a slight permanent precipitate is produced. Then 150 grams of caustic potash is added, and the solution made up to a litre in volume.

impure. When about one-third of the water has been distilled, the middle third may be collected, and is free from both soluble and volatile impurities if proper precautions are taken in the distillation.

Even distilled water becomes impure if freely exposed to the air, for it dissolves the atmospheric gases and traces of the other impurities in the atmosphere. Pure distilled water is now made on a large scale, and sold to the public under various names after aeration with carbon dioxide.

What we have learnt

In our fourteenth Lesson we have studied water as a solvent, and noticed the influence of temperature on the amount of a solid which can be dissolved in water. It was noticed that solids are usually more soluble at higher than at lower temperatures, whilst gases are less soluble.

When the solutions of two salts are mixed together, *precipitation* takes place, when they can produce an insoluble or difficultly soluble compound by their mutual decomposition. Many metallic salts combine with water, and the compounds thus produced are capable of existing in the solid state as crystals. We have seen that the volume of a gas (measured at a constant pressure) which can be dissolved by water is proportional to the pressure at which the solution is effected. The air dissolved in water is of the utmost importance for the preservation of all forms of aquatic animal life. The most important characters of rain water, spring, river, and sea water have been mentioned, whilst the causes of temporary and permanent hardness in water have been explained,—the former being due principally to the presence of the bicarbonates of lime and magnesia, and the latter to their sulphates or chlorides.

It was seen that temporary hardness could be removed by boiling, or by precipitation with lime (Clark's process), whilst permanent hardness could not be removed by these means, but could be removed by the addition of sodium carbonate.

The various methods of purifying water from its suspended and dissolved impurities, such as subsidence, softening, precipitation, filtration, and distillation, have been explained.

Exercises on Lesson XIV

1. What is the effect of temperature on the solubility of (1) a solid, (2) a gas? What is the effect of pressure on the solubility of a gas?

2. Explain the precipitation which often takes place when the solution of two salts are mixed together.

3. Give the formulæ and common names of several salts which contain water of crystallisation.

4. What are the chemical characters of the various natural waters?

5. Of what importance is the dissolved air in natural waters?

6. Explain the hardness of water, both temporary and permanent, state how such waters may be softened, and give equations for the reactions.

7. Explain fully how you would prepare pure water from a muddy river water.

8. Is distilled water always pure? If not, why not?

9. What is meant by efflorescence and deliquescence?

10. What weight of anhydrous sodium carbonate is contained in 1000 grams of washing soda?

11. A liquid which is given to you is stated to be water. By what experiments would you demonstrate that the liquid is really water? [Its specific gravity, freezing and boiling points, solvent action on salts, etc. colour, taste, and chemical reactions should be described.]



LESSON XV

NITROGEN AND AIR

PRESSURE, TEMPERATURE, HUMIDITY, AND EXTENT OF THE ATMOSPHERE—THE BAROMETER—CHEMICAL COMPOSITION AND ANALYSIS OF AIR—ACTION OF ANIMALS AND PLANTS ON THE AIR—VENTILATION.

Nitrogen

SYMBOL N. ATOMIC WEIGHT 13.94. DENSITY 13.94

Occurrence.—As we have seen (p. 9), nitrogen occurs in the free state in the air, of which it forms four-fifths by volume. Nitrogen exists in the state of combination in nitre or saltpetre, potassium nitrate, KNO_3 (whence the element derives its name). It forms an essential constituent of the bodies of all animals and plants.

Preparation.—(1) Nitrogen can be prepared (see Expt. 9) by burning phosphorus in a closed volume of air, the oxygen being entirely removed; after the white fumes of phosphorus pentoxide (P_2O_5) have disappeared, the colourless gas remaining is nearly pure nitrogen (see Fig. 62).

(2) To obtain it perfectly pure, air which has been dried and freed from carbonic acid is passed over metallic copper turnings in a long glass tube heated to redness, when oxide of copper remains in the tube and pure nitrogen passes over and may be collected in a pneumatic trough.

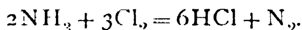
(3) Nitrogen gas can also be obtained by heating certain of its compounds. Thus if a concentrated solution of am-

monium nitrite (NH_4NO_2) be heated, nitrogen is evolved whilst water is eliminated.



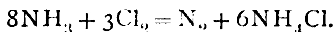
$$(NH_4)NO_2 = N_2 + 2H_2O.$$

(4) Ammonia, a compound of nitrogen and hydrogen (NH_3), is decomposed by chlorine, with formation of hydrochloric acid and liberation of nitrogen :—



$$2NH_3 + 3Cl_2 = 6HCl + N_2.$$

If a current of chlorine gas be passed through a saturated solution of ammonia the reaction as above stated occurs, and nitrogen can be collected as usual. The hydrochloric acid formed unites with the excess of ammonia forming sal-ammoniac (NH_4Cl).



$$8NH_3 + 3Cl_2 = N_2 + 6NH_4Cl.$$

Care must be taken, in making this experiment, that ammonia always remains in excess, otherwise an explosive compound is produced.

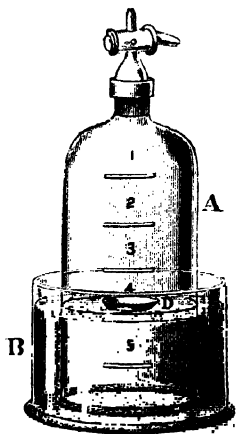


Fig. 62.

Properties. — Although nitrogen does not support combustion and is an inert gas, yet it can be made to combine with both oxygen and hydrogen ; with both elements it unites to form a strong acid, viz. nitric acid, HNO_3, and with the latter it combines to form a powerful base, ammonia, NH_3. At a very low temperature and under a high pressure, nitrogen condenses to a colourless liquid which boils about -193°. Nitrogen acts as a diluent to the atmospheric oxygen, and although it does not support life, it is not poisonous, animals brought into nitrogen dying of suffocation from want of oxygen ; indeed, it is clear that nitrogen cannot exert an injurious effect on the animal, as it is inhaled in large quantities at every inspiration.

NITROGEN AND OXYGEN

The Atmosphere

Experiments described in the foregoing lessons have shown us that the air or atmosphere (ατμός vapour, σφαῖρα a sphere) which surrounds the earth consists of oxygen and nitrogen gases present in the proportion of about 1 to 4 by volume. It now becomes necessary to study the properties as well as the composition of the air more closely, and in the first place the question of the weight of the air claims attention.

Weight of the Air.—This can readily be shown by removing the air, by means of an air-pump, from a glass globe, the neck of which is furnished with a stopcock, hanging the vacuous globe on one arm of a balance, and placing weights to equipoise the system in the pan attached to the other arm. On then opening the stopcock, the air will be heard to rush in and the equilibrium will be destroyed, the arm of the balance to which the globe is attached descending. The weight of the air has been very exactly determined by a process similar to that above described, but carried out with every precaution, so that the errors of experiment are reduced to as small an amount as possible. These determinations show that one litre of dry air at 0° C. and under a pressure of 760 mm. at the sea's level at London (latitude 51° 28′) weighs 1.293 grams.

Pressure of the Atmosphere.—The atmosphere thus possessing weight, must exert a pressure on every object on the earth's surface, and therefore upon the human body. But inasmuch as the pressure of the air is exerted, under ordinary conditions, in all directions equally, we do not feel it. If, however, we place the hand so as to close the top of a glass cylinder, open at both ends, setting the other end firmly on the plate of an air-pump which is then worked so as to withdraw the air from within the cylinder, the fact of the weight or pressure of the air becomes very evident and we shall feel some difficulty in removing the hand. If a piece of bladder be tied over the mouth of the cylinder instead of the

hand being placed on it, it will be found that as the air is abstracted from beneath, the bladder bulges inwards and at last bursts with a loud noise owing to the pressure of air upon it. As the air is an elastic fluid, it obeys Boyle's law of pressures (see p. 53), that is, its density is directly proportional to the pressure to which it is subjected. Hence, as we ascend from the sea's level, the density of the air becomes less, a portion of the superincumbent pressure being removed. At the sea's level the average pressure of the atmosphere is equal to that of a column of mercury of 760 mm. or 29.922 inches, and as mercury is 13.5 times as heavy as water, the air can sustain a column of water of 32 feet. This pressure amounts to 103.3 kilos on every square centimetre or 14.73 lbs. per square inch. The human body has, therefore, to sustain a pressure of several tons, and if this pressure be suddenly reduced, as when rapid ascents are made in balloons, the effect of the diminution is observed in hæmorrhage from the nose, mouth, and eyes, consequent upon the bursting of small blood-vessels in those parts. The same elevation may be attained by gradual means, as by ascending a mountain, without evil effects resulting, as the blood-vessels then have time to accommodate themselves to the new conditions.

The Barometer.—In the seventeenth century a Florentine pump-maker found that an ordinary lift-pump would not raise water more than 32 feet. In 1643 Torricelli gave the true explanation by making a simple experiment. Taking a glass tube 3 feet in length, closed at one end, and filling it with mercury he closed the open end with his thumb, and then inverted the tube in a basin filled with mercury. The mercury then sank in the tube till the column was about 760 mm. in height, at which point it remained stationary. Above this level was an empty space which is still called the Torricellian vacuum. He next poured water on to the top of the mercury contained in the basin, and raised the tube so that the open end came into the water. The mercury then flowed out and the water rushed up, completely filling the tube. Thus the *barometer* was discovered, but this name was given to it by Robert Boyle. In order to test the accuracy of the explanation of the suspension of the mercury in the tube

being due to the atmospheric pressure, Pascal determined to ascertain whether the mercury in the barometer sank when the instrument was taken up a mountain. Unable to do this himself, he commissioned his brother-in-law Périer to make the trial, and this he did on the Puy-du-Dôme. The mercury continued to sink as he ascended the mountain until he reached the summit, when it remained at a constant level.

The sinking of the barometric column as the superincumbent pressure is removed is shown by a simple experiment. Here I have a barometer-tube (Fig. 63) filled with mercury; I invert it in a basin of mercury and we see that the mercury sinks to a certain level, the space above being a vacuum. Now a tubulated receiver is brought over the tube, a perforated india-rubber stopper surrounding the tube and fitting tightly into the tubulus of the receiver, the whole being placed on the plate of an air-pump. As the air in the receiver is pumped out, we notice that the level of the mercury in the tube gradually sinks, until at last it is nearly on the same level as the mercury in the basin. On slowly opening the stopcock of the pump, air rushes in to fill the empty receiver, and the mercury in the tube is seen gradually to rise until it reaches the point at which it stood before the experiment.

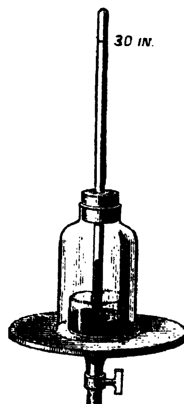


Fig. 63.

The variation in the height of the barometer with elevation above the sea's level can be employed to determine the amount of that elevation. When the mercury sinks one-tenth of an inch, the elevation reached is about 90 feet, but for this purpose the cumbersome mercurial barometer is generally discarded in favour of a little pocket *aneroid* barometer which is about as large as an ordinary watch, and in which no mercury is used. The variations in pressure cause an index to move over a graduated dial. In making mercurial barometers care must be taken to exclude all air or other gas from the tube, as the pressure of even a trace greatly impairs the instrument. It is therefore necessary to boil the mercury in the tube so as to expel all air adhering to the glass or to the mercury.

Variation in Height of the Barometer.—As the atmosphere is in constant motion, its pressure at the same spot undergoes changes, and these are indicated by corresponding changes in the height of the barometer, and as a change of atmospheric pressure usually accompanies change of weather, the variations of the barometer indicate approaching change of meteorological conditions. Hence the use of the barometer as a weather-glass.

Extent of the Atmosphere.—As the density of the air diminishes as the distance from the sea's level increases, it is difficult to say exactly to what height it extends. But there is no doubt that a limit exists beyond which there is no air. The height at which the air still possesses sensible density is calculated to be from 40 to 45 miles. Suppose the earth to be represented by a globe one foot in diameter, the atmosphere will be represented by a film of air $\frac{1}{12}$ of an inch thick. If the air were of the same density throughout, it would only reach to a height of rather more than 5 miles above the sea's level.

Temperature of the Air.—Like its density, the temperature of the air varies greatly at different places, and at different heights over the same place. It diminishes everywhere as we ascend into higher regions, and at last we come to a point where the temperature never rises above the freezing point. This is called the line of perpetual snow. Under the equator this line is not reached until we rise above 15,000 feet; in our own latitude it is reached at a height of about 4000 feet, whilst in the latitude of 75° it comes down to the sea's level. The atmosphere acts not only as a powerful modifier of the sun's heat, but as an equally powerful retainer and distributer of that heat. Were it not for the presence of the air, the earth's surface would be scorched by day and frozen by night.

Air a Mixture, not a Compound.—In the first place let us discuss the question, Is the air a compound of oxygen and nitrogen, or a mere mechanical mixture? For some time chemists were doubtful what answer to give. Now, there is no doubt that air is a mechanical mixture, and not a chemical compound, and for the following reasons:—

(1) When gases combine heat is given out, and often an alteration of bulk takes place. If we mix oxygen and nitrogen

in the proportion in which they occur in air, no evolution of heat or change of bulk can be noticed, and the mixture acts in every respect like air.

(2) Gases combine in the ratio of their atomic weights, or in multiples of these; the ratio between oxygen and nitrogen in the air is not that of the combining weights of oxygen and nitrogen, or in multiples thereof.

(3) Although the composition of the air is nearly constant as regards the proportion of oxygen to nitrogen, yet it is not exactly so; small but perceptible variations occur. No such variations could be observed if these gases were combined in air to form a chemical combination.

(4) And most convincing proof. If we shake up air with water, the water absorbs some of the air; if we take the water thus saturated with air, and boil it, the dissolved air will escape. The air which thus escapes can be collected and analysed. This has often been done, and it is found that the quantity of oxygen contained in the air which has been dissolved by the water is in larger proportion to the nitrogen in the same dissolved air than it was in the original atmospheric air. Thus, whilst the percentage of oxygen in the air taken is nearly 21, that in the air obtained by boiling the water is nearly 34.

	Air undissolved in Water.	Air dissolved in Water.
Oxygen	20.96	33.64
Nitrogen	79.04	66.36
	100.00	100.00

This change in the proportion of nitrogen to oxygen from 4 : 1 to nearly 2 : 1, could not occur if the air were a compound, as the compound would be dissolved *as a whole;* it would not be decomposed by simply shaking it up with water, and then the relative proportion between the two gases would remain, after boiling out, the same as it was before, viz. 4 to 1.

The above numbers exactly agree with the solubilities of oxygen and nitrogen separately. Oxygen is found to be more soluble than Nitrogen.

(5) Another convincing proof is that when air is liquefied by great cold and pressure, it is found that gaseous nitrogen is first given off from the liquid, and after a while the gas

which is slowly evolved contains sufficient oxygen to ignite a glowing chip. Thus the liquefied air behaves as a mechanical mixture of the two elements, one of which (nitrogen) is more volatile than the other. Hence we have five reasons for regarding air as a mechanical mixture of its two chief constituents.

How Air is Analysed.—If we wish to determine with accuracy the composition of the atmosphere, we must use more exact methods than those described in the foregoing lessons. First, as regards oxygen and nitrogen. Chemists use for this purpose two methods,—one to ascertain exactly the weights of oxygen and nitrogen present, the second to measure with accuracy the volumes of these two gases present in air; for

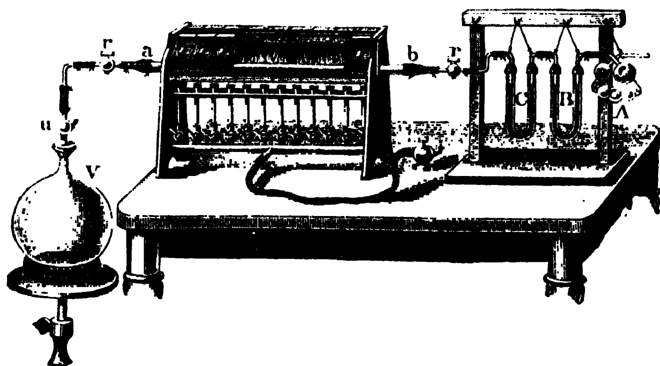


Fig. 64.

both methods the air must be previously freed from all other ingredients.

Analysis of Air by Weight.—This method depends on the fact that oxygen gas is absorbed by heated metallic copper with formation of oxide of copper, CuO, whilst nitrogen gas is not thus absorbed. Fig. 64 shows the form of apparatus used for this purpose. The glass globe V, furnished with a stopcock *u*, is rendered vacuous by the air-pump, and, after being carefully weighed, is attached to a tube of difficultly-fusible glass (*ab*) which is furnished with two stopcocks (*rr*); this is also carefully weighed after having been filled with bright copper turnings. This tube is connected at the one end

with the empty globe, and at the other with a series of tubes and bulbs (C, B, and A). These serve to free the air from carbonic acid, by means of the bulbs, which contain a strong solution of caustic soda; and from aqueous vapour, by means of the U tubes (B and C), which contain pumice stone soaked in strong sulphuric acid, a substance which absorbs aqueous vapour greedily. The weighed tube containing the copper is then heated to dull redness by the Bunsen burners fixed in the gas furnace. Next, the stopcocks *rr* and *u* are slightly opened when the air of the room in which the experiment is made, or that brought from a distance in a glass globe and attached to the bulbs (A), passes over the hot copper, which thereby is oxidised, and the air thus completely deprived of its oxygen, whilst the nitrogen passes unabsorbed into the globe V. As soon as the experiment is finished, and the tube allowed to cool, both the globe and the cool tube are weighed. The increase in weight of the globe gives the weight of the nitrogen, whilst that of the tube gives that of the oxygen. In an experiment of this kind carried out with very great care, the weight of oxygen obtained was found to be 3.680 grams; that of the nitrogen being 12.373 grams. Hence the percentage composition of air by weight is: O 23.005 per cent; N 76.995 per cent; and many repetitions of this experiment proved that the 100 parts by weight of air contains almost exactly 23 parts of oxygen to 77 parts of nitrogen.

As we know the relative densities of oxygen and nitrogen it is easy to calculate from the above numbers the composition of air by *volume*, and we find that O = 20.77 per cent and N = 79.23 per cent. Hence, comparing the two results, we have—

Composition of the Air

	By Volume.	By Weight.
Oxygen	20.77	23.005
Nitrogen	79.23	76.995
	100.00	100.00

Composition of Air by Volume.—But it is necessary that we should have the means of determining the composition by volume experimentally. For this purpose we employ an

instrument called a Eudiometer (from εὐδία clear weather, and μέτρον a measure—a measure of the clearness or purity of the air, or of the quantity of oxygen which it contains). The arrangement used is shown in Fig. 46, p. 93.

The eudiometer A, a strong tube closed at one end, and carefully graduated in millimetres, is first completely filled with mercury, and such a volume of the air to be examined is allowed to enter as will fill about $\frac{1}{6}$ of the eudiometer. This volume is then accurately read off by a telescope on the divided millimetre scale of the eudiometer, the height of the barometer and that of the thermometer as well as that of the column of mercury in the eudiometer above the level of the mercury in the trough being also ascertained for the reasons given on p. 93. Next, a volume of pure hydrogen, more than enough to combine with all the oxygen contained in the air taken, is added, and the volume of air plus hydrogen carefully ascertained with all the precautions already mentioned. The open end of the eudiometer is then firmly held on a thick sheet of india-rubber under the mercury, and an electric spark passed through the gases by means of a battery and induction coil, which passes the spark through the gas by two platinum wires fused into the sides of the tube at its upper end. Combination of the hydrogen with the oxygen of the air occurs in the eudiometer, water being formed. The eudiometer is then raised from the india-rubber block, when the mercury is seen to rise in the tube, showing that a diminution of volume has taken place; this is accurately measured as before. To what is this due? It is caused, as we have learnt (p. 92), by the union of exactly two volumes of hydrogen with one volume of oxygen, to form liquid water, which occupies so small a space, compared with that of the constituent gases, as to be inappreciable. Therefore, the volume of oxygen contained in the air under examination must be one-third of the diminution in volume which has been observed as a consequence of the combination. If I took exactly 100 volumes of air, and added 50 volumes of hydrogen, and I found 87 volumes after the explosion, or a diminution of 63 volumes, then $\frac{63}{3} = 21$ would be the volume of oxygen contained in 100 volumes of air, the other 79 being nitrogen.

Example

Air employed (vols. corrected to NTP) . .	428.93
Air + hydrogen	749.77
After the explosion	480.09
Diminution in volume (= water H_2O) . . .	269.68
Oxygen corresponding to diminution = $\frac{1}{3}$ diminution	89.89 = 20.96 O
Air − oxygen = nitrogen	339.04 = 79.04 N
	100.00

Results of Air Analyses as regards Oxygen and Nitrogen.—A large number of eudiometric analyses of air made at different times at the same locality, and at different localities, have shown that although the proportion of 21 volumes of oxygen to 79 of nitrogen may be taken as giving the average composition of pure air, yet differences are observed which lie outside the errors of experiment. The variation ranges from 20.9 to 21.0, and in the air of towns, and especially in mines, the amount of oxygen may sink as low as 20.3. The low percentage of oxygen, 20.77, found by the gravimetric method must be taken as being not so accurate as that obtained by the volumetric method, 20.96, as there are slight unavoidable experimental errors in the former, which are got rid off in the latter method.

EXPT. 63. **Carbonic Acid in the Air.**—If lime-water or baryta-water * is poured into a shallow dish, and exposed to the air for half an hour, it will be noticed, on pouring it into a test glass, that it has become turbid, and that white particles are floating about in the liquid. As this is the test we previously used to detect carbonic acid gas (or carbon dioxide) the experiment shows that this gas is present in atmospheric air, and we have already learnt that fires and the breathing of animals produce it. It is only present, however, in minute

* Lime-water is made from quicklime, CaO, by pouring water over it so as to slake it, in which operation heat is evolved, owing to the chemical combination between the lime and water. $CaO + H_2O = Ca(OH)_2$. Slaked lime or calcium hydrate, $Ca(OH)_2$, dissolves slightly in water, and a clear solution is obtained on shaking up some of the hydrate in water and allowing the excess to subside. The clear solution may be poured off after a few hours, and kept in a well-stoppered bottle for use. Baryta-water is similarly prepared.

quantities, and that is the reason why lime-water, poured into a jar of ordinary air, does not at once become turbid.

Pure country air contains only about 3 to 4 parts of CO_2 per 10,000 parts of air by volume. In towns where much coal is burnt, especially if there is no wind, this amount may rise to 6 or 7 parts; whilst in badly ventilated and crowded rooms, in which gas is also being burnt, the proportion may reach as much as 20 or 30 parts.

Methods of Estimating the Amount of CO_2 in Air.—The amount of CO_2 in air can be found by aspirating a definite volume of dried air (not less than 20 litres) through U tubes and bulbs filled with caustic potash, KOH; this absorbs

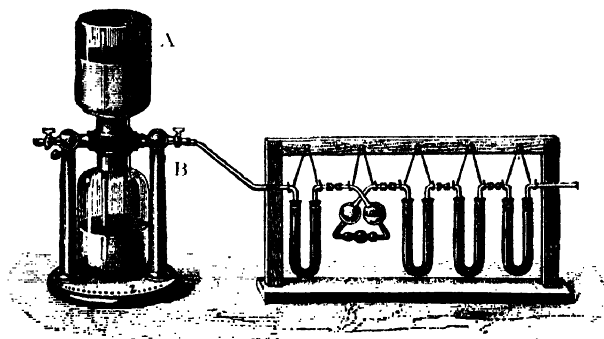
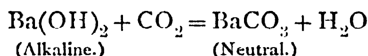


Fig. 65.

CO_2, and forms potassium carbonate, K_2CO_3. $2\ KOH + CO_2 = K_2CO_3 + H_2O$. The tubes are weighed before and after the experiment, and the amount of carbonic acid absorbed is thus found. Fig. 65 shows the apparatus employed. A is an aspirator, consisting of two large glass bottles movable on a horizontal axis. The upper one is filled with water, which, as it flows into the lower one, draws after it an equal volume of air which passes through the series of tubes and stopcock B. The first tube contains pumice stone, moistened with strong sulphuric acid, whilst the second is filled with dry calcium chloride; these absorb all the aqueous vapour before the air passes through the next U tube, in which most of the carbonic acid is absorbed; the air next bubbles through a strong solution of caustic potash in the absorption bulbs, and passes, last

of all, through another tube filled with small pieces of caustic potash, which ensures that no loss of water vapour takes place from the bulbs.

Pettenkofer's Method of Estimating CO_2 in Air.—This method is much more convenient and more easily carried out than the foregoing, and is generally used. A large cylindrical stopped glass bottle, holding 10 litres or more, is used. This is filled with the air to be examined, and a measured volume of baryta-water of known strength is added. After shaking the liquid with the air, and allowing it to stand for half an hour, the whole of the CO_2 is absorbed.



$$Ba(OH)_2 + CO_2 = BaCO_3 + H_2O$$
(Alkaline.) (Neutral.)

Half the volume of liquid is now taken out by means of a pipette, and the amount of baryta remaining in solution is found by adding a solution of oxalic acid of standard strength until all the *free* baryta is neutralised. The baryta and oxalic acid solutions are made of such a strength that equal volumes of each will neutralise (see p. 83) each other, and so that 1 c.c. of baryta will absorb (say) 1 c.c. of CO_2.

Example

Volume of air taken for analysis	10 litres.
,, baryta solution added (1 c.c. solution = 1 c.c. CO_2 NTP)	50 c.c.
,, oxalic acid solution required to neutralise 25 c.c. of the turbid baryta	22 c.c.
,, baryta solution combined with CO_2 $(25-22)\times 2 =$	6 c.c.
,, CO_2 in 10,000 c.c. of air (10 litres) = 6 c.c. or 6 parts per 10,000.	

Water Vapour in the Air.—We have evidence of the presence of aqueous vapour in the air in the occurrence of dew, hoar frost, snow, and rain. A shallow dish full of water, if placed in the open air in summer, quickly evaporates into the air, and similar evaporation is constantly taking place from the sea, lakes, and rivers. If we bring a cold bright mirror into a warm room, the mirror becomes dimmed and bedewed with moisture. A person wearing spectacles in the open air in winter finds, on coming into a warm gas-lit room, that his spectacles are dimmed so much as to render them temporarily

useless; this is because the cold glass has condensed the water vapour present in the air of the room, and caused an artificial deposition of dew.

The quantity of water which can be taken up by the air depends upon the temperature. At high temperatures air can take up a much larger amount of water as gas than at low temperatures. If warm moist air be cooled, it soon reaches a temperature at which it can no longer retain all its aqueous vapour as a gas, and this is deposited as liquid water. The air is then said to be saturated, and the temperature at which this occurs is called the *dew-point.* This deposition of liquid water takes place readily when minute particles of dust are present, and thus mist and fog are formed. Warm air ascending from the sea, and heavily charged with water vapour, reaches a height at which the temperature is low enough to condense part of the water into clouds. If now these are blown into a much colder region, a further condensation takes place, and rain is produced. If one cubic mile of air, saturated with water at 35° C., be cooled to 0°, it will deposit upwards of 140,000 tons of water as rain. If the condensation takes place in an atmosphere below the freezing point, snow or hail is produced. Snow is water vapour which has assumed the crystalline form in condensing in a cold atmosphere. Fig. 66 shows the various forms of snow crystals. When condensation takes place at the cold surface of the earth, on clear summer nights, dew is formed; whilst, if the surface of the earth is below 0° C., a similar condensation takes place as hoar frost. One cubic metre of air can take up of water vapour,

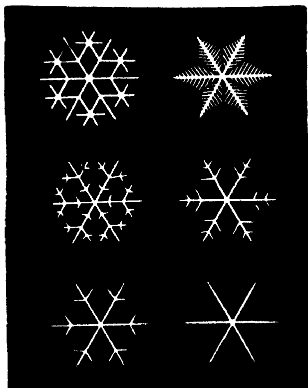


Fig. 66.

At	0° C.	4.871 grams.	At	20° C.	17.157 grams.
,,	5° C.	6.795 ,,	,,	30° C.	30.095 ,,
,,	10° C.	9.362 ,,	,,	40° C.	50.700 ,,
,,	15° C.	12.746 ,,	,,	100° C.	588.73 ,,

Estimation of Water Vapour in Air.—The increase in weight of the first two U tubes (Fig. 65), used in the estimation of CO_2 in air, gives also the amount of water present in the volume of air experimented with. A more simple method of ascertaining the amount of moisture in the air consists in the use of the wet and dry bulb hygrometer. It consists merely of two sensitive thermometers placed side by side (Fig. 67), the bulb of one is surrounded by a piece of muslin which is constantly kept moist by a strand of the muslin dipping into a little vessel full of distilled water. Evaporation of water is constantly taking place from the moist muslin round the bulb. When water evaporates, heat is absorbed, and when the air is very dry the evaporation is rapid, and consequently the thermometer indicates a much lower temperature than that of the air, as indicated by the dry-bulb thermometer. If the air be saturated with water vapour no further evaporation takes place, and both thermometers register the same temperature. From this "hygrometric break," or difference between the two thermometers, the amount of aqueous vapour present in the air can be computed from hygrometric tables. For other methods depending on the determination of the "dew-point," a work on physics must be consulted.

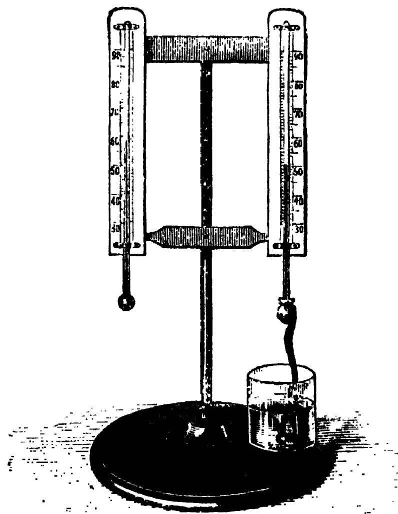


Fig. 67.

Equilibrium of Chemical Composition of the Air—Action of Animals and Plants.—Our bodies are constantly undergoing a slow combustion ; the air which we expire is laden with carbonic acid gas and water vapour, owing

to the combustion or slow oxidation of the carbon and hydrogen of our bodies by the oxygen of the air. To prove this, we have only to breathe against a bright mirror, when it instantly becomes dimmed owing to the water vapour condensing to minute drops of water. Similarly, if we breathe through a glass tube into a little lime-water, it soon becomes milky, showing the presence of carbonic acid gas. It may be asked, Why is it that all the fires burning, and all the animals breathing, do not use up the oxygen in the air, the amount of which, in fact, is not found to diminish? The answer is that the oxygen of the air is constantly being renewed, and the CO_2 diminished by the action of plants, the green parts of which contain *chlorophyll*, which has the power of decomposing CO_2 in presence of sunlight, using the carbon * for the building up of its tissues, and liberating the oxygen for the use of man and animals. Thus we see that what is poison to man is the necessary food of plants, and whilst oxygen is a necessity of life for man, it is a mere bye-product of the life-processes of plants. Both processes, then, tend to produce an equilibrium in the chemical composition of the air.

Organic Matter in the Air.—The motes which are seen dancing in the sunbeam are particles so small, that except when illuminated by the sunlight, they are not only invisible, but float in the air and are always more or less present in the atmosphere, except at great elevations. These motes contain minute particles of mineral matter, and also microscopic living organisms or their germs. These latter cannot, in strictness, be called chemical constituents of the air, and yet as they play a most important part in bringing about chemical changes, their existence and mode of action cannot be ignored even in elementary lessons on chemistry. These microbes or their germs cause such liquids as milk, beer, wine, etc. to turn sour on standing in the air. Exclude these microscopic organisms from the air, and these liquids remain sweet for any length of time, even when exposed to air, if thus purified; give the

* The tissues of plants contain large quantities of *carbohydrates*, or compounds which contain carbon combined with hydrogen and oxygen in the proportions in which they are combined in water, *e.g.* cellulose and starch, $C_{12}H_{20}O_{10}$; cane sugar, $C_{12}H_{22}O_{11}$; grape sugar (glucose) and fruit sugar (levulose), $C_{12}H_{24}O_{12}$.

organisms entrance, and the liquids soon turn sour. Fortunately most of the organisms which float in the air are not specially hurtful to animal life, but certain so-called "pathogenic" or "disease" germs exist, and these are sometimes present in the air, and may give rise to disease.

Ventilation.—The importance, for the due preservation of health, of breathing as pure air as possible, especially in-doors, cannot be too strongly insisted upon, and the chemist has found that, when the amount of carbonic acid reaches 7 in 10,000 of air, that air is not wholesome, not so much because this quantity of carbonic acid is hurtful, as because when this amount is reached in dwelling-rooms or work-shops where human beings live or work, harmful exhalations from the body as well as microbic organisms are present, which exert a deteriorating influence on the health. Hence it is necessary for the well-being and comfort of those inhabiting such rooms that a proper and continual renewal of the air should occur, and to effect this without creating unpleasant draughts is the object of a sound system of ventilation.

If a number of people breathe the air, or if a candle flame be burning in a closed space where there is no means of ventilation, *i.e.* no outlet for impure air nor inlet for pure air, then that space becomes so laden with carbon dioxide that the people are suffocated, and the candle flame at last will not burn.

Expt. 64.—This experiment shows the need of ventilation in order to support the flame of a candle. A candle is placed in a glass dish which contains a layer of water, a narrow lamp chimney is now placed over the flame (Fig. 68), but as no air can enter the tube at the bottom, and as the products of combustion rise and prevent fresh air from entering at the top, the flame soon goes out. If now we relight the flame, and replace the lamp

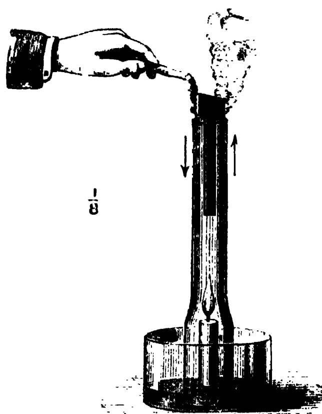


Fig. 68.

glass, but this time furnished with a cardboard partition, we shall find that the flame continues to burn, because the heated products of combustion can rise up one-half of the chimney and fresh air can enter down the other, as may be shown by holding a piece of smouldering brown paper near the inlet.

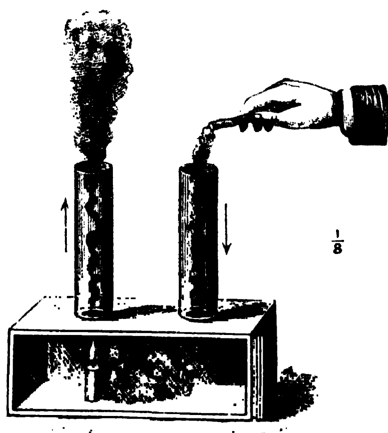


Fig. 69.

One of the most important means of ventilating dwelling-rooms is the chimney, which usually contains a column of heated air, which ascends, being lighter than the air outside, whilst fresh air enters the room through every crevice or by means of the imperfect fitting of doors or windows, but preferably by properly constructed inlets.

Expt. 65.—Fig. 69 shows an experiment which will illustrate this: one side of a box is removed and replaced by a sheet of glass, two holes are bored in the upper side of the box and these are covered with wide glass tubes. A lighted candle is placed under one of the tubes, and the heated air and products of combustion, being lighter than the surrounding air, ascend through it, whilst the colder and heavier air passes down the other tube to take its place, as may be seen by holding a piece of smouldering brown paper over the cold air inlet.

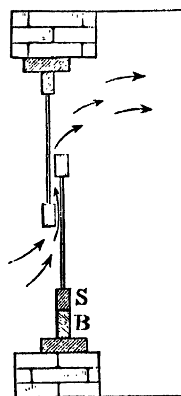


Fig. 70.

It is in this manner that coal-mines are ventilated. The box in the figure may be compared to the workings of the mine, and the two tubes to the upcast and downcast shafts which ventilate the mine, a large fire being lighted at the bottom of the upcast shaft.

Thus a fire in a room is not only useful for its warmth, but also for its ventilating action. When gas-lights are burning, and people are breathing in a room, the hot and impure air ascends to the top of the room, as may easily be proved by standing on the table and breathing the upper layers of air. Hence, an outlet for these hot and impure gases should be provided by means of a suitable grating placed either in the outside wall, or leading into the chimney at points just below the ceiling. An inlet for fresh pure air should also be provided either by a grating in the outer wall below the level of the floor boards, or by raising the lower sash S of the window a few inches, and fitting a long piece of wood, B, in the lower aperture ; this allows fresh air to enter the space between the two sashes as shown in Fig. 70, and purifies the air of the room without creating a draught, as the fresh air enters at a level at which it will not be felt.

What we have learnt

In the fifteenth Lesson we have studied the various methods of preparing nitrogen and examined its most characteristic properties. We have considered the most important facts regarding the atmosphere, viz. its weight and pressure, its extent and temperature.

We have seen that the air is a mechanical mixture and not a chemical compound of nitrogen and oxygen, and have learnt the methods by which air is analysed, not only as regards its principal components, nitrogen and oxygen, but also as regards carbon dioxide and moisture. The effects of animal and vegetable life upon the atmosphere have been considered, and it was shown that each tends to support an equilibrium in the chemical composition of the air. Lastly, the principles of ventilation have been touched upon, and illustrated by various experiments.

Exercises on Lesson XV

1. Explain the various methods of preparing nitrogen.
2. What is the action of chlorine on ammonia?
3. Describe several experiments to show the weight and pressure of the atmosphere.
4. Write out an account of the various reasons for regarding air as a mixture and not a compound of nitrogen and oxygen.

5. Describe the experiments, both volumetric and gravimetric, by which the composition of air has been ascertained.

6. How is the amount of atmospheric carbon dioxide and water vapour ascertained gravimetrically?

7. Explain the effects of animal and plant life on the composition of the atmosphere.

8. Describe experiments which illustrate the necessity for ventilating dwelling-rooms.

9. Explain the action of the wet and dry bulb thermometer.

10. What is the proportional amount of CO_2 existing in the open air; what is the proper limit in the air of rooms?

11. Explain the formation of dew, rain, hoar frost, and snow.

12. In what respect does air dissolved in water differ from atmospheric air?

LESSON XVI

COMPOUNDS OF NITROGEN AND OXYGEN

N_2O, N_2O_2, N_2O_3, N_2O_4, and N_2O_5

NITROUS ACID, HNO_2, NITRIC ACID, HNO_3

THE NITRITES AND NITRATES

Nitric acid, HNO_3

THE starting-point for all the above compounds is nitre or saltpetre, KNO_3, potassium nitrate, from which compound nitric acid, HNO_3, is obtained. All the oxides of nitrogen may be prepared from nitric acid, and for this reason it will be treated first.

Preparation.—Nitric acid is prepared by acting with sulphuric acid, H_2SO_4, on nitre, KNO_3, or on Chili saltpetre, $NaNO_3$, thus



$$KNO_3 + H_2SO_4 = KHSO_4 + HNO_3.$$

EXPT. 66.—In order to prepare nitric acid on a small scale, about equal parts of dry nitre crystals and concentrated sulphuric acid are placed in a stoppered retort and gently heated by a Bunsen burner (Fig. 71). The nitric acid distils over and is collected in a flask which is kept cool by a stream of cold water. The residue in the flask contains potassium hydrogen sulphate, $KHSO_4$, or bi-sulphate of potash. On the large scale, Chili saltpetre, $NaNO_3$, a salt which is found as vast deposits in Chili, is used because it is cheaper. The salt is placed in a large iron cylinder, heated by a fire, and

closed at the end by a circular stone flag, through a hole in which a large earthenware pipe is inserted for the purpose of carrying off the vapour of the acid to the condensers.

Properties.—Nitric acid is a strongly fuming liquid, possessing a sharp acrid smell, and is colourless when pure, but is usually slightly tinged yellow, owing to the presence of oxides of nitrogen. It is a very corrosive substance, and hence it is sometimes called *aqua fortis*. When concentrated it burns the hands, and causes painful wounds, but if more dilute it only stains the hands yellow. As its formula shows, it contains 76 per cent of oxygen, and it acts as an energetic oxidising agent. This is seen by bringing a few copper turnings or a small piece of metallic tin into a test-tube containing a little of the acid. Red fumes are at once given off and the metals are oxidised, the tin to tin dioxide, SnO_2, and the copper to copper nitrate, $Cu(NO_3)_2$. In the same way, if strong nitric acid be poured upon sawdust, torrents of red fumes are emitted, and so much heat is given off that the sawdust is frequently inflamed.

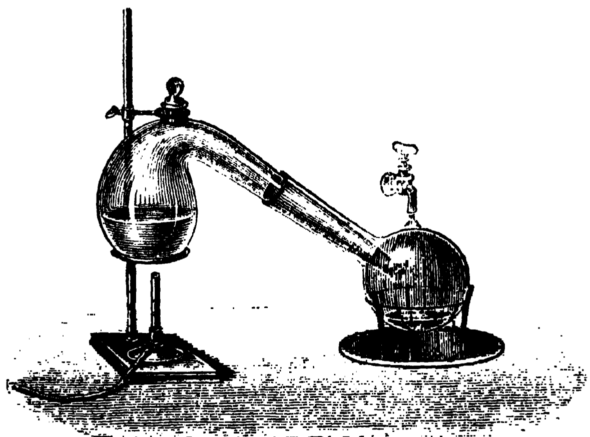


Fig. 71

Tests for Nitric Acid.—In all cases, the *salts* of nitric acid (nitrates) must be mixed with concentrated sulphuric

acid so as to liberate the nitric acid before the following tests can be applied.

EXPT. 67.—(1) Copper turnings added to the acid, and the mixture warmed, give rise to dense red fumes possessing a characteristic smell, whilst the solution is turned blue owing to the formation of copper nitrate in solution. (2) A more delicate test consists in mixing the substance with concentrated sulphuric acid in a test-tube, cooling the mixture, and then pouring carefully down the sides of the tube on to the surface of the mixture, a solution of ferrous sulphate (green vitriol), $FeSO_4$, when a dark brownish-black ring forms at the surface where the liquids meet if a nitrate or nitric acid be present. This is known as the ring test. (3) Blue indigo solution is at once decolorised by nitric acid.

Uses.—Nitric acid is largely used in the arts and manufactures for dissolving silver, large quantities of silver nitrate being now used for photographic purposes. It is employed for making coal-tar colours, for preparing nitro-glycerine and gun-cotton, as well as collodion for photographic use. It is used also for etching on copper, and in the manufacture of sulphuric acid (see p. 207).

The Nitrates

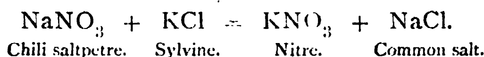
The nitrates may be considered as nitric acid in which the hydrogen has been replaced by a metal, or group of elements equivalent to a metal, *e.g.*—

HNO_3	KNO_3	$(NH_4)NO_3$.
Nitric acid (or Hydrogen nitrate).	Potassium nitrate.	Ammonium nitrate.

Occurrence.—Although nitric acid itself does not occur in the free state in nature, its salts are widely distributed in the soil, and vast deposits of sodium nitrate, $NaNO_3$, are to be found in Chili, whence its name Chili saltpetre. When nitrogenous animal matter is buried in the soil, the water draining from that soil is found to contain nitrates. The formation of these salts depends upon the action of certain minute organisms called bacteria, which have the power of converting the ammonia, given off during the decomposition of the

animal matter, into nitrous acid (HNO_2) and nitric acid (HNO_3) or their salts.

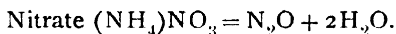
Preparation.—In India and other hot countries, the nitrates which are thus produced from decomposing organic matter occur as an efflorescence on the surface of the soil, and it is the work of a certain caste of the natives (Sorawallahs, from *sora*, nitre) to collect and purify the crude product by crystallisation. After recrystallisation, the salt is ready for sale. Potassium nitrate is now obtained on a large scale by the double decomposition of Chili saltpetre, with the naturally occurring potassium chloride (sylvine) found in large quantities at Stassfurt.



$$\underset{\text{Chili saltpetre.}}{NaNO_3} + \underset{\text{Sylvine.}}{KCl} = \underset{\text{Nitre.}}{KNO_3} + \underset{\text{Common salt.}}{NaCl}.$$

The common salt is first deposited as crystals, whilst the mother-liquor contains the nitre which crystallises out afterwards.

Properties.—All nitrates are soluble in water, and when ignited usually decompose with the evolution of red fumes of the higher oxides of nitrogen, whilst oxides are left behind. Potassium nitrate, on heating strongly, is converted partially into the nitrite, KNO_2, oxygen being evolved, whilst ammonium nitrate decomposes into nitrous oxide and water.



$$\text{Nitrate } (NH_4)NO_3 = N_2O + 2H_2O.$$



$$\text{Nitrite } (NH_4)NO_2 = N_2 + 2H_2O.$$

As we have seen, the nitrite, containing one atom of oxygen less in the molecule than the nitrate, evolves nitrogen under similar circumstances.

EXPT. 68.—The oxidising action of nitre can be well shown by fusing some of the salt in a round-bottomed hard glass flask, and dropping into it a small piece of charcoal; the carbon immediately bursts into flame, and continues to burn brilliantly until it is consumed by the oxygen in the nitre.

Uses.—Potassium nitrate, KNO_3, is chiefly used as an oxidising agent, as it contains a very large proportion [47 per cent] of oxygen. It is therefore used in the manufacture of gunpowder and fireworks. It is also used in medicine and in the

pickling of meat. Chili saltpetre, $NaNO_3$, is used in the manufacture of sulphuric acid (see p. 207), and as a manure, whilst silver nitrate, $AgNO_3$, is used largely in photography, for the preparation of the chloride, bromide, and iodide of silver. Lead nitrate, $Pb(NO_3)_2$, ferric nitrate, $Fe_2(NO_3)_6$, and aluminium nitrate, $Al_2(NO_3)_6$, are used in dyeing and calico printing, whilst strontium nitrate, $Sr(NO_3)_2$, and barium nitrate $Ba(NO_3)_2$, are used for producing the crimson and green lights of pyrotechnic displays.

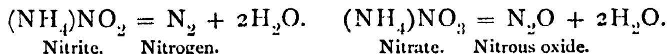
THE OXIDES OF NITROGEN

Nitrogen Monoxide or Nitrous Oxide

FORMULA N_2O. MOLECULAR WEIGHT 43.7. DENSITY 21.85

Laughing Gas.—Nitrous oxide is sometimes called laughing gas, because when mixed with air and inhaled, it produces a peculiar and transient intoxicating effect, and if inhaled in the pure state for a short time, it acts as an anæsthetic, that is, renders the person insensible to pain for a few minutes. It is, therefore, used for dental operations. This gas does not occur naturally.

Preparation.—(1) We have already seen (under nitrogen) that when ammonium nitr*ite* is decomposed by heat, nitrogen gas and steam are evolved. In the same way ammonium nitr*ate*, prepared by neutralising nitric acid with ammonia, thus $HNO_3 + NH_3 = (NH_4)NO_3$, a compound which contains one more atom of oxygen in the molecule, gives off nitrous oxide when decomposed by heat, thus



$$\underset{\text{Nitrite.}}{(NH_4)NO_2} = \underset{\text{Nitrogen.}}{N_2} + 2H_2O. \quad \underset{\text{Nitrate.}}{(NH_4)NO_3} = \underset{\text{Nitrous oxide.}}{N_2O} + 2H_2O.$$

EXPT. 69.—Place about 20 grams of dry nitrate of ammonium in a flask furnished with a wide delivery tube, as used in the preparation of oxygen (Fig. 72). Heat the salt until it begins to decompose, and then regulate the flame of the lamp, otherwise the gas is evolved too rapidly. The pneumatic trough must be filled with warm water, because the gas

dissolves considerably in cold, but to a less extent in hot water.

(2) Nitrous oxide may also be obtained by the action of very dilute nitric acid on zinc, or other metals.

Properties.—Nitrous oxide is a colourless gas, possessing a pleasant smell and sweet agreeable taste. It is condensed to a colourless liquid under a pressure of 32 atmospheres at 0°. Poured into an open vessel the liquid is cooled down by its own evaporation to a temperature of $-100°$ C. Nitrous oxide has also been obtained in the solid state. Potassium and sodium take fire in this gas with formation of their peroxides, whilst the nitrogen is set free.

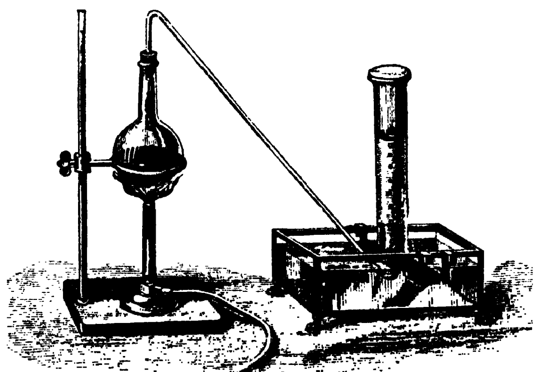


Fig. 72.

Experiments with Nitrous Oxide

Expt. 70.—Collect a test-tube full of the gas, and insert a glowing chip; it will at once burst into flame, just as in the case of oxygen.

Expt. 71.—Having collected several jars of the gas, proceed as with oxygen, to burn phosphorus in a deflagrating spoon; the phosphorus will burn almost as brightly as in oxygen.

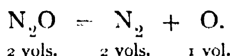
Expt. 72.—If a piece of sulphur, well alight, is introduced into the gas it continues to burn almost as brightly as in oxygen, but if only feebly burning, the flame is put out. The reason of this is that the gas must first be decomposed

into its constituent elements, nitrogen and oxygen, before it can act as a supporter of combustion, and to effect this decomposition a tolerably high temperature is necessary.

EXPT. 73.—Charcoal also burns as in oxygen.

EXPT. 74.—Even a steel watch spring burns as in oxygen, if tipped with brightly-burning sulphur.

Nitrous Oxide as a supporter of Combustion.—It is evident from the above experiments that nitrous oxide must first be decomposed into nitrogen and oxygen before bodies can burn in it, but we may ask, Why is it that this mixture of nitrogen and oxygen does not act as ordinary air, which is also a mixture of the same two gases? Let us inquire what would be the composition by volume of the mixture produced by the decomposition of nitrous oxide.



$$\underset{\text{2 vols.}}{N_2O} = \underset{\text{2 vols.}}{N_2} + \underset{\text{1 vol.}}{O.}$$

From the above equation we see that two volumes of the gas yield, on decomposition, two volumes of nitrogen and one volume of oxygen, so the mixture contains *one-third* or 33.3 per cent of oxygen, whereas atmospheric air only contains *one-fifth* or 20 per cent of oxygen; and it is to this larger proportion of oxygen that nitrous oxide owes its powers as a supporter of combustion.

Distinguishing test for Nitrous Oxide and Oxygen.—The method by which these two gases may be distinguished from each other will be better understood after considering nitric oxide, and will be given under that gas, see p. 158.

Determination of Composition of Nitrous Oxide.—(1) If a small piece of potassium is heated in a bent tube containing a measured volume of the gas, over mercury (Fig. 73), the metal takes fire, combining with all the oxygen and liberating the nitrogen, and it is found that the volume of nitrogen left is the same after the experiment as the volume of gas

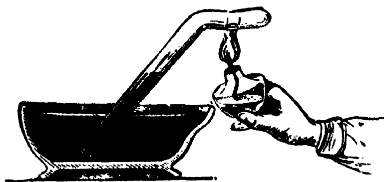


Fig. 73.

taken. Therefore nitrous oxide contains its own volume of nitrogen.

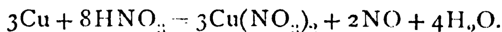
(2) The density of nitrous oxide has been carefully determined, and it is found to be nearly 22 times as heavy as hydrogen, therefore two volumes weigh 44; but of this, 2 volumes or 28 parts are nitrogen, hence the rest $(44 - 28 = 16)$ is oxygen. Therefore we have 2 atoms (2×14) of nitrogen and one atom of oxygen (16) in the molecule, and the density (22) is half the molecular weight (44). These experiments give the formula N_2O to this gas.

Nitrogen Dioxide or Nitric Oxide

FORMULA * NO. MOLECULAR WEIGHT 29.8. DENSITY 14.9

Nitric oxide does not occur naturally.

Preparation.—(1) Nitric oxide is best prepared by the action of strong nitric acid on metallic copper; the following equation expresses the reaction,



$$3Cu + 8HNO_3 = 3Cu(NO_3)_2 + 2NO + 4H_2O.$$

EXPT. 75.—Copper turnings are introduced into a flask so as to well cover the bottom, and these are covered with water; strong nitric acid is then added through the thistle funnel (Fig. 74), when an evolution of gas begins. It will be noticed that the flask is first filled with a dark reddish-brown gas, but this colour soon disappears and a colourless gas is seen to be evolved, and collects in the gas jars.

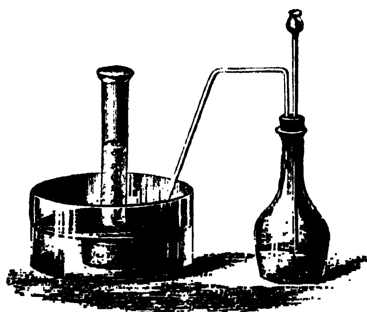


Fig. 74.

The red colour first noticed is due to the fact that nitric oxide has the power of combining with the oxygen of the air, which the flask first contains,

* See determination of composition of nitric oxide, p. 158.

to form the higher oxides, N_2O_3 and N_2O_4, which have a red colour, but the air in the flask is soon used up or expelled, and the gas is then seen to be colourless.

EXPT. 76.—The gas thus obtained is, however, not pure, but contains free nitrogen and nitrous oxide. To obtain it in the pure state the gas prepared as above must be led into a cold concentrated solution of ferrous sulphate, $FeSO_4$ (green vitriol), with which it forms a peculiar compound of a deep blackish-brown colour. It is this compound which is produced in the ring test for nitrates. When this deep-coloured solution is heated the pure gas is given off.

Properties.—Nitric oxide is a colourless gas which, on coming in contact with atmospheric air or oxygen, combines with the latter to form red fumes of the higher oxides, N_2O_3, and N_2O_4 (see Expts. 77 and 78). It is not easily condensed to a liquid, as it requires a pressure of 104 atmospheres at a temperature of -11° C. The gas is decomposed by heated metallic potassium, which combines with the oxygen and liberates the nitrogen.

Experiments with Nitric Oxide.—Having collected several jars of the gas prepared by the first method, we will make the following experiments.

EXPT. 77.—Remove the cover from one of the jars and expose the gas to the air. Deep brownish-red fumes (N_2O_3 and N_2O_4), possessing a characteristic and disagreeable acrid suffocating smell, are noticed.

EXPT. 78.—Pass oxygen into a second jar of the gas whilst still on the shelf of the pneumatic trough; deep red fumes are produced as before, but these quickly disappear, as they are very soluble in water. If the oxygen be added gradually to the pure gas, and in the proper proportion, *all* the gas will disappear owing to the red fumes dissolving in the water.

EXPT 79.—Phosphorus burns brilliantly in nitric oxide, but only when it is already brightly burning when brought into the gas. The flame of feebly-burning phosphorus, as well as those of sulphur and of a candle, are, on the other hand, extinguished on plunging them into nitric oxide, because the temperature of these flames is not sufficiently high to decompose this gas into its elementary constituents.

EXPT. 80.—If a few drops of carbon disulphide, CS_2, be

poured into a cylinder full of the gas and shaken so as to allow the vapour to mix with it, it will be found that the mixture is very inflammable and burns, on applying a light, with a splendid blue and intensely luminous flame which is very rich in chemically active rays.

Test for Nitric Oxide and distinguishing Test for Nitrous Oxide and Oxygen.—The above experiments (77 and 78) will explain how free oxygen may be used as a test for nitric oxide, and this latter gas has been used not only as a test for free oxygen but also as a means of estimating its amount, and it was formerly used for the analysis of air. We now, however, possess better methods (see Air, p. 137). Nitrous oxide does not form red fumes with nitric oxide as oxygen does; they may thus be distinguished from each other although they both answer the glowing chip test for oxygen.

Determination of Composition of Nitric Oxide.—The composition of nitric oxide is ascertained in the same way as that of nitrous oxide, viz. by heating a small piece of metallic potassium in a measured volume of the gas over mercury (Fig. 75).

(1) It is found that the volume of nitrogen liberated is only *half* that of the nitric oxide taken. (2) The density of nitric oxide is found to be nearly 15, therefore 2 volumes weigh 30, but this volume contains only 1 volume or 14 parts by weight of nitrogen, therefore the oxygen is 30 − 14 = 16 parts. This shows that the compound contains one atom of nitrogen combined with one atom of oxygen in the molecule, and its density (15) therefore is half its molecular weight (30).

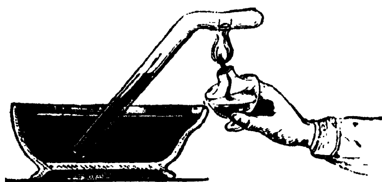


Fig. 75.

But why is the formula NO given to nitric oxide instead of N_2O_2 which we have previously used for nitrogen *di*-oxide?

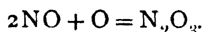
Because if we use N_2O_2 for the molecular formula then this gas will be an exception to the law (p. 55) that *the density of any compound gas is half its molecular weight.* The density being 15, the molecular weight, according to this

law, is 30 and the formula is NO. It is as though the single molecule N_2O_2 had split up into two molecules of NO. The name nitrogen *di*-oxide is given to this gas because for the same weight of nitrogen it contains twice as much oxygen as nitrogen *mon*-oxide. The remaining three oxides of nitrogen need only be considered here very shortly.

Nitrogen Trioxide

FORMULA N_2O_3. MOLECULAR WEIGHT 75.5. DENSITY 37.7

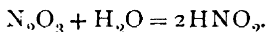
This gas is formed together with the tetroxide when nitric oxide is exposed to the air or oxygen. It is obtained when a mixture of 4 volumes of nitric oxide and 1 volume of oxygen is allowed to pass through a hot tube.



$$2NO + O = N_2O_3.$$

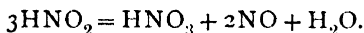
Nitrogen trioxide is a dark-red gas and is easily condensed by a freezing mixture to a deep blue liquid at the ordinary pressure of the air, but even at $-2°$ the liquid trioxide is unstable, decomposing with liberation of nitric oxide.

Nitrous Acid, HNO_2.—Nitrogen trioxide is an acid-forming oxide, and combines with ice-cold water to form nitrous acid.



$$N_2O_3 + H_2O = 2HNO_2.$$

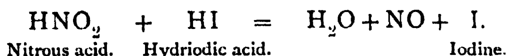
Nitrous acid is a very unstable substance, and has not been prepared in the pure state. Even its aqueous solution rapidly undergoes decomposition when heated, giving rise to nitric acid and nitric oxide thus—



$$3HNO_2 = HNO_3 + 2NO + H_2O.$$

The Nitrites or salts of nitrous acid are, on the other hand, very stable bodies; they are all soluble in water and give off red fumes of N_2O_3 when treated with an acid.

Test for Nitrites.—If a solution of a nitrite be added to a mixture of boiled starch with potassium iodide acidified with acetic acid, iodine is liberated and the starch is turned blue.



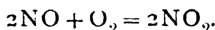
$$\underset{\text{Nitrous acid.}}{HNO_2} + \underset{\text{Hydriodic acid.}}{HI} = H_2O + NO + \underset{\text{Iodine.}}{I}.$$

This reaction serves as a very delicate test for a nitrite, and is useful in testing water for nitrites, which may be taken as evidence of the previous contamination and gradual decomposition of animal matter.

Nitrogen Tetroxide or Nitrogen Peroxide

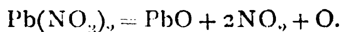
FORMULA NO_2. MOLECULAR WEIGHT 45.7. DENSITY 22.8

Nitrogen peroxide has already been mentioned as being formed together with the trioxide. It may be prepared by mixing four volumes of nitric oxide with two volumes of oxygen and leading the red fumes into a tube surrounded by a freezing mixture.



$$2NO + O_2 = 2NO_2.$$

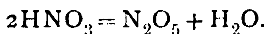
It may also be formed by the decomposition of lead nitrate by heat.



$$Pb(NO_3)_2 = PbO + 2NO_2 + O.$$

It may also be prepared by heating nitric acid with arsenic trioxide, As_2O_3—a mixture of nitrogen trioxide and peroxide is evolved which is condensed in a tube surrounded by a freezing mixture; by passing oxygen through this liquid the trioxide is oxidised to tetroxide. Nitrogen tetroxide solidifies to colourless crystals at $-9°$, slightly above this temperature the liquid also is colourless, but at $10°$ it attains a decided yellow colour which darkens further at higher temperatures.

Nitrogen Pentoxide or Nitric Anhydride (N_2O_5).—This compound is a white crystalline solid obtained by removing the elements of water from nitric acid by means of phosphorus pentoxide, P_2O_5, a substance which has a great power of abstracting water.



$$2HNO_3 = N_2O_5 + H_2O.$$

Nitrogen pentoxide is an unstable body, and is not used in the arts; it is interesting as being the highest oxide of nitrogen, and the *anhydride* of nitric acid, uniting with great energy with water to form this acid.

What we have learnt

In the sixteenth Lesson we have learnt the method of preparing nitric acid, nitrates, and the five oxides of nitrogen, and the mode of showing their properties and composition experimentally.

Nitric acid is prepared from nitre and sulphuric acid, nitrous oxide from ammonium nitrate, and nitric oxide by the action of nitric acid on copper.

Exercises on Lesson XVI

1. How is nitric acid prepared? How would you proceed to show its properties?
2. How is nitre prepared from Chili saltpetre?
3. What is the result of strongly heating (*a*) ammonium nitrite, (*b*) ammonium nitrate?
4. Why is nitrous oxide a good supporter of combustion? How would you distinguish it from oxygen?
5. I want 12 litres of nitric oxide at 14° C. and 738 mm. How much copper and nitric acid must I take?
6. How can you prove that the formulæ N_2O and NO represent the composition of nitrous and nitric oxide? Why is NO called nitrogen dioxide?
7. How would you test a sample of water for nitrites?
8. What volume of nitrous oxide at 15° C. and 770 mm. can I get by decomposing 400 grams of ammonium nitrate, and what volume of oxygen at NTP does the gas contain?
9. How is nitrogen pentoxide prepared? Give an equation showing its action upon water.
10. What is laughing gas; how is it prepared?
11. Why is the formula NO_2 given to nitrogen tetroxide?
12. A white crystal is said to be nitre; how would you ascertain whether this is so or not?
13. What weight of sylvine is required to decompose completely one ton of Chili saltpetre, and how much nitre will be theoretically formed?

LESSON XVII

COMPOUNDS OF NITROGEN AND HYDROGEN, AMMONIA (NH_3), AND THE AMMONIUM (NH_4) COMPOUNDS

NITROGEN combines with hydrogen to form three compounds: (1) Ammonia, NH_3. (2) Hydrazine or diamide, N_2H_4. (3) Azoimide, N_3H. Of these the first is the most important and is the only one which we shall here study.

Ammonia

FORMULA NH_3. MOLECULAR WEIGHT 16.9. DENSITY 8.45

We have learnt that the animal body contains substances into which nitrogen enters as a component part; certain portions of plants, especially the fruit, seeds, and juice, also contain nitrogenous compounds. Now, whenever these nitrogenous materials, whether of plants or of animals, are decomposed either naturally in the air or by heating them, ammonia is given off. The peculiar pungent smell of this compound is noticed if we heat a bit of cheese in a test-tube, and its presence can be further shown by thrusting a piece of moistened red litmus paper into the test-tube, when the red colour will be changed to blue, for ammonia is a gas which has an alkaline reaction. This same smell is often noticed in urinals and stables, showing that animal nitrogenous matter has there been converted into ammonia. A common name for ammonia is spirits of hartshorn, this substance having, in former days, been prepared by heating horn. Again, the name ammonia is

derived from the temple of Jupiter Ammon in the Libyan desert, because it was there that the Arabs first prepared a salt of ammonia—Sal-ammoniac—by heating dry camel's dung.

Ammonia is now almost exclusively obtained as a bye-product in the destructive distillation of coal in making coal-gas, where it collects as ammoniacal liquor. This liquor is neutralised by hydrochloric acid, and on evaporation a solid salt is obtained known as Sal-ammoniac, NH_4Cl (a compound of ammonia, NH_3, and hydrochloric acid, HCl), and from this compound ammonia gas can be readily prepared.

Preparation.—Ammonia gas is obtained in the laboratory by heating sal-ammoniac with lime.

EXPT. 81.—A mixture is made of two parts of powdered quicklime and one part of sal-ammoniac. This is placed in a flask and covered with a layer of dry quicklime, CaO, which serves to absorb the moisture given off during the decomposition.



$$\underset{\text{Lime.}}{CaO} + \underset{\text{Sal-ammoniac.}}{2(NH_4)Cl} = \underset{\text{Calcium Chloride.}}{CaCl_2} + \underset{\text{Ammonia.}}{2NH_3} + H_2O.$$

The mixture is heated, and the gas led off by a delivery tube as in Fig. 76.

Ammonia gas cannot be collected over water because of its great solubility; with water it forms spirits of hartshorn or liquor ammoniæ of the shops; but it can be collected over mercury, or, more simply, by upward displacement (see Fig. 76).

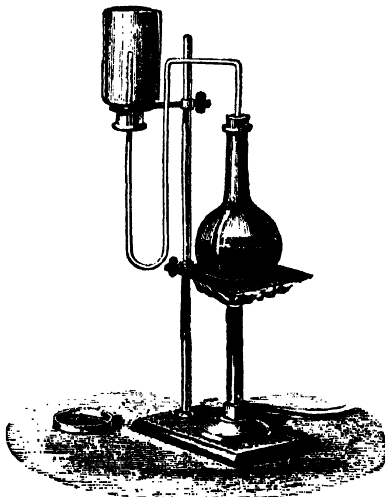


Fig. 76.

EXPT. 82.—To ascertain when the jar is filled with ammonia it is only necessary to hold a stopper or glass rod moistened with strong hydrochloric acid below the mouth of the bottle, and if the jar is full, and ammonia gas is escaping,

dense white fumes of sal-ammoniac will be seen to form round the stopper ($NH_3 + HCl = NH_4Cl$).

Properties.—Ammonia is a colourless gas possessing a peculiar pungent odour well known as that of smelling salts, which contain it. When the pure gas is inhaled or the strong liquid swallowed death often ensues. It is lighter than air, its density being 0.59 (air = 1). It is exceedingly soluble in water, one volume of water absorbing 1148 vols. of the gas at 0°, whilst at 20°, 741 vols. of the gas are absorbed under a pressure of 760 mm.

EXPT. 83.—If a jar of the gas is brought under the surface of water contained in the pneumatic trough, on removing the cover the water is seen to rush up and fill, or nearly fill, the jar, according as the whole or only a part of the atmospheric air has been expelled by the ammonia gas.

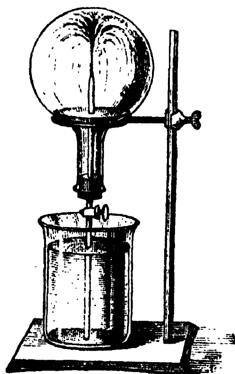


Fig. 77.

EXPT. 84.—A better way of showing this is to fill a round-bottomed flask with the gas by displacement, and insert a stopper, through which passes a piece of glass tubing, ending in a jet passing up into the middle of the flask, and outwards for about a foot so as to dip into a beaker of water (Fig. 77). On cooling the gas by dropping a small quantity of ether on the outside of the flask, a little water enters. This dissolves so much gas that the pressure inside the flask is greatly reduced, and the water rushes into it in the form of a fountain. If the water in the beaker be first coloured red with litmus, the alkaline character of the solution may be demonstrated by the change of colour to blue as the liquid enters the flask.

EXPT. 85.—If the delivery tube be allowed to dip into a bottle half filled with distilled water, it will be noticed that although the gas may be bubbling through the wash-bottle very rapidly, yet no gas passes through the water (Fig. 78), as all the bubbles are absorbed almost as soon as they reach the liquid. In this manner the aqueous solution is prepared. The

saturated solution of ammonia is lighter than water, and has a specific gravity of about 0.880.

Ammonia gas can be liquefied by exposure either to cold (about -34°), or to pressure (about 7 atmospheres at the usual temperature of the air), and the liquid freezes to an ice-like solid if further cooled below -75°. Ammonia does not support combustion under ordinary circumstances, but if mixed with oxygen and a light applied to the end of the tube from which the mixed gases escape, the hydrogen of the ammonia unites with oxygen and the mixture burns with a bright flame tinged yellow by the presence of the nitrogen, which, however, does not burn.

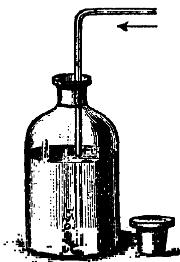


Fig. 78.

Ammonia Freezing Machine.—We have seen on p. 108 that when steam is condensed to water the large amount of heat necessary for the existence of the gaseous condition becomes free, and *vice versâ*, that when water is converted into steam heat is absorbed (see p. 109). The same thing happens (to a greater or less extent) whenever a gas becomes a liquid or a liquid a gas; and this can be made use of in the case of ammonia for the artificial production of ice. All that is needed is to have two strong iron vessels connected together with a pipe; into one of these (the retort) is placed an aqueous solution of ammonia saturated at 0°, and the whole made air-tight. If we wish to make ice, the water to be frozen is placed in the inside of the second vessel (the receiver) which is hollow, and this vessel plunged into a bucket of cold water. Heat is now applied to the retort, the effect of this is to drive out the ammonia gas from the solution, this passes over into the receiver and

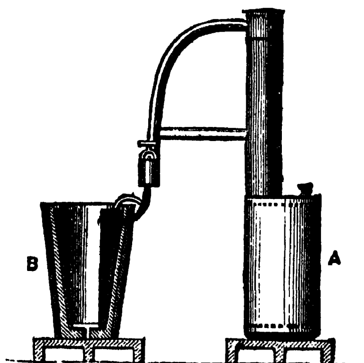
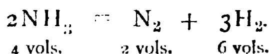


Fig. 79.

gradually collects there until the pressure of the accumulated gas becomes so great (about 10 atmospheres) as to cause liquefaction of the ammonia. The liquid ammonia then collects in the hollow receiver. As soon as the aqueous solution in the retort has become hot and has given off the greater part of its ammonia, the position of the vessels is altered; the retort is placed in cold water, and the receiver in the air, but surrounded with flannel. What takes place now? A reabsorption of ammonia in the cooled water begins, and a consequent evaporation of the liquid ammonia in the receiver, so much heat being absorbed in this evaporation that the water placed in the inside of the receiver is frozen. This process can be made continuous on a large scale, and thus tons of water can be frozen at a comparatively small cost. It will be seen that thus by burning coal we make ice.

EXPT. 86. **Composition of Ammonia.**—If we pass a series of electric sparks through a measured volume, say 40 c.c., of dry ammonia gas collected in a eudiometer (see p. 93) over mercury, the volume of the gas is seen to become greater, until at last no further increase takes place. On measuring the gas we now find that the volume is exactly double what it was to begin with, *i.e.* 80 c.c. This is because the ammonia has been decomposed into its elements, viz. nitrogen and hydrogen.



$$\underset{4\text{ vols.}}{2NH_3} = \underset{2\text{ vols.}}{N_2} + \underset{6\text{ vols.}}{3H_2}.$$

If we now add a measured quantity of oxygen sufficient to combine with all the hydrogen, to form water when a spark is passed into the mixed gases, the diminution in bulk which follows the passage of the spark is due to the formation of liquid water, and for this, as we know, 2 volumes of hydrogen unite with 1 of oxygen (p. 94). We find in our experiment that this loss of volume amounts to 90 c.c., of which $\frac{2}{3}$ or 60 c.c. must be hydrogen. Therefore there must have been $80 - 60 = 20$ volumes of nitrogen. Hence 40 volumes of ammonia contain 20 volumes of nitrogen and 60 of hydrogen, or 2 volumes contain 1 volume of nitrogen and 3 volumes of hydrogen, and NH_3 represents the composition of ammonia.

EXPT. 87.—Another method of showing the composition

of ammonia consists in filling with chlorine a long glass tube closed at one end, and stoppered at the other, the stoppered end communicating with a smaller stoppered tube (Fig. 80). The stopper dividing the tube into two portions is not pierced through, but contains a cavity capable of holding a few drops of liquid.

When the long tube is completely filled with chlorine, it is divided into three equal portions by elastic bands fitting tightly on the tube, and a strong solution of ammonia is placed in the upper short portion, and the stopcock is turned so as to admit a few drops of it to the lower tube. The entrance of the ammonia is accompanied by a small lambent yellowish-green flame at the point where the drop enters the gas. This is due to a combination between the hydrogen of the ammonia with the chlorine to form hydrochloric acid, nitrogen being liberated. When ammonia has been added drop by drop until all the chlorine has disappeared, a little sulphuric acid is introduced in the same way as the ammonia was, so as to absorb the excess of ammonia gas. We know, however (p. 181), that chlorine combines with its own volume of hydrogen to form hydrochloric acid, and therefore we must have used the same volume of hydrogen as we took of chlorine to commence with. It only now remains to find out what is the volume of nitrogen remaining, and this is easily done by inverting the tube in water and taking out the stopper, when water enters the tube to fill the partial vacuum, and on equalising the pressure inside and outside the tube, it is seen that the nitrogen remaining occupies just one-third the length of the tube, showing that 1 volume of nitrogen had been combined with 3 volumes of hydrogen.

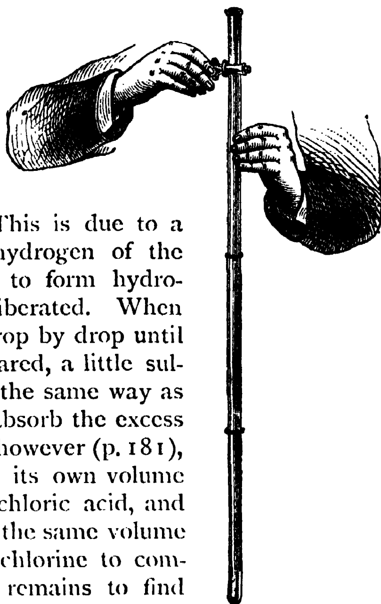
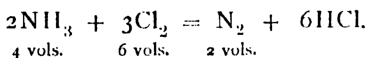


Fig. 80.



$$\underset{4\ \text{vols.}}{2NH_3} + \underset{6\ \text{vols.}}{3Cl_2} = \underset{2\ \text{vols.}}{N_2} + 6HCl.$$

The Ammonium Salts.—Ammonia unites with acids to form salts, called the salts of *ammonium*. Because these salts so closely resemble the salts of the alkali metals, potassium and sodium, ammonia is termed the volatile alkali. The analogy in constitution of the salts of ammonia with those of potash and soda is exhibited by supposing that the former contain a component NH_4 (ammonium), which acts like the metals K or Na. Thus, if we write sal-ammoniac $NH_3.HCl$, the analogy which exists between it and potassium chloride, KCl, is not evident; whilst if we represent the first salt by the formula $(NH_4)Cl$, in which NH_4 displaces K, the analogy is at once seen. So we have—

Salts of Potassium.	Salts of Ammonium.
Potassium chloride, KCl	Ammonium chloride $(NH_4)Cl$
Potassium sulphate, K_2SO_4	Ammonium sulphate $(NH_4)_2SO_4$
Potassium nitrate, KNO_3	Ammonium nitrate $(NH_4)NO_3$

The quasi-metal—that is, a body acting like a metal, but not really one—has not been obtained in the free state.

What we have learnt

In the seventeenth Lesson we learnt how to prepare ammonia by heating sal-ammoniac with lime and collecting the gas by upward displacement, as it is lighter than air. We have seen that the principal properties of ammonia are its solubility in water, and its alkaline properties enabling it to neutralise acids to form ammonium salts, which are analogous to the corresponding potassium salts, and contain the group of atoms (NH_4) which acts like a metal, and is called ammon*ium*.

We have learnt two methods of demonstrating the composition of ammonia, viz. (1) by decomposing the gas by electric sparks in a eudiometer, and then finding the amount of nitrogen and hydrogen produced, by exploding the mixture with an excess of oxygen; (2) by gradually adding strong ammonia solution to a measured volume of chlorine, which combines with the hydrogen bulk for bulk and liberates a volume of nitrogen equal to one-third the bulk of the chlorine. The ammonia freezing machine has also been described, and its mode of action explained.

Exercises on Lesson XVII

1. How would you prepare ammonia gas, and demonstrate its most characteristic properties?

2. What is the action of ammonia on (1) hydrochloric, and (2) sulphuric acid, (3) chlorine, (4) water? Give equations.

3. I want 10 litres of ammonia gas at NTP ; what weight of ammonium chloride must I use?

4. Describe in detail two methods by which the composition of ammonia can be ascertained.

5. Describe and explain the action of the ammonia freezing machine.

6. Write down the formulæ of several ammonium compounds, and show their analogy to the potassium compounds.

7. How would you demonstrate the great solubility of ammonia gas in water?

8. From what source is ammonia derived on a large scale?

9. What is the weight of 746 c.c. of ammonia gas measured at 10° C. and 760 mm.?

10. What is the volume of ammonia (NTP) which, when passed into 4 grams of pure H_2SO_4 of 50 per cent strength, will neutralise the acid?

11. What volume of nitrogen at 14° R. and 560 mm. will be left after acting with ammonia on 486 c.c. of chlorine at 5° C. and 780 mm.?

LESSON XVIII

CHLORINE, HYDROCHLORIC ACID, AND THE CHLORIDES

Chlorine*

SYMBOL Cl. ATOMIC WEIGHT 35.2. DENSITY 35.2

CHLORINE gas was first obtained and its properties examined by Scheele in 1774; he prepared it by the action of hydrochloric acid, HCl, on manganese ore, containing the dioxide, MnO_2.

Sir Humphry Davy in 1810 first satisfactorily proved the elementary nature of the gas and gave it its present name from its colour, χλωρός, greenish-yellow.

Occurrence.—Chlorine does not occur in the free state in nature, but its compounds are widely diffused; thus common salt, which is present in such large quantities in sea-water, is sodium chloride, NaCl; rock salt also has the same composition. Potassium chloride, KCl, or sylvine is found in large quantities as a natural deposit at Stassfurt in Germany. Other chlorides will be mentioned under "The chlorides."

Preparation.—(1) Chlorine gas is easily prepared by the action of strong hydrochloric acid, HCl, on black oxide of manganese, manganese dioxide, MnO_2, manganese chloride being also produced.



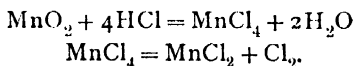
$$MnO_2 + 4HCl = MnCl_2 + 2H_2O + Cl_2.$$

This reaction depends on the formation, in the first instance, of manganese tetrachloride, $MnCl_4$, for when manganese dioxide and cold concentrated hydrochloric acid are brought in contact,

* The elements bromine and iodine belong to the same group of elements as chlorine, and are closely analogous in their properties.

Bromine is a dark-red liquid, which gives off a vapour at the ordinary temperature of the air, having a very penetrating and unpleasant odour. Bromine boils at 59° C., furnishing a dark brownish-red gas. Iodine is a heavy crystalline solid, having a glistening metallic appearance. It also gives off vapour slightly at the ordinary temperature of the air, and this smells like very dilute chlorine. When heated it gives off a beautiful dark-violet vapour, see Expt. 8, p. 5.

a dark-brown solution is formed which, on heating, decomposes into manganous chloride and chlorine, thus—



$$MnO_2 + 4HCl = MnCl_4 + 2H_2O$$
$$MnCl_4 = MnCl_2 + Cl_2.$$

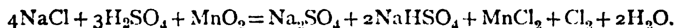
Fig. 81.

This process is employed for the manufacture of chlorine on a large scale for making bleaching powder.

EXPT. 88. The apparatus used for the preparation of chlorine in the laboratory is shown in Fig 81. The manganese dioxide in small lumps is first introduced into the large flask and well covered with the strong acid. The flask is connected by a

delivery tube bent twice at right angles with a wash-bottle (*b*) half filled with water, to absorb the vapour of hydrochloric acid which is carried over with the chlorine ; it next passes through strong sulphuric acid in wash-bottle *a*, and along the inclined tube containing pumice stone moistened with strong sulphuric acid, which serves to deprive the gas of aqueous vapour. The gas is then collected in the gas jar *c*, by downward displacement, as it is about two and a half times as heavy as air, and is soluble in water. The tube *d*, which dips under caustic soda solution, acts as a safety-valve in case the evolution of gas becomes too rapid. It is easily seen when the gas jar is full of the gas, by its green colour. As chlorine has a very irritating and poisonous effect on the nose, mouth, and throat, *this experiment and all others with chlorine, should be made in a "draught chamber,"* as shown in Fig. 81, so arranged that the apparatus can be enclosed by a sliding glass door, and all fumes carried away to a flue leading to the chimney.

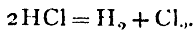
(2) It is sometimes convenient to generate the hydrochloric acid from common salt, NaCl, and strong sulphuric acid, H_2SO_4, in intimate contact with the manganese dioxide. In this reaction the hydrochloric acid first formed is at once decomposed by the manganese dioxide with evolution of chlorine, thus—



$$4NaCl + 3H_2SO_4 + MnO_2 = Na_2SO_4 + 2NaHSO_4 + MnCl_2 + Cl_2 + 2H_2O.$$

EXPT. 89.—In this method 11 parts by weight of common salt are mixed with 5 parts of manganese dioxide, and 14 parts of sulphuric acid, diluted with an equal bulk of water, are added. On gently heating the mixture, chlorine is given off regularly.

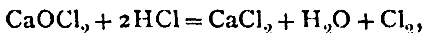
(3) Chlorine may also be prepared by the electrolysis of hydrochloric acid.



$$2HCl = H_2 + Cl_2.$$

(See determination of composition of hydrochloric acid, p. 179).

(4) Chlorine gas is evolved when an acid such as hydrochloric or sulphuric is added to bleaching powder, $CaOCl_2$ (see p. 185), thus—

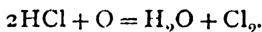


$$CaOCl_2 + 2HCl = CaCl_2 + H_2O + Cl_2,$$



$$CaOCl_2 + H_2SO_4 = CaSO_4 + H_2O + Cl_2.$$

(5) When a mixture of air and hydrochloric acid gas (HCl) is strongly heated, the hydrogen of the acid is oxidised to water by the oxygen of the air, whilst chlorine is liberated, thus—



$$2HCl + O = H_2O + Cl_2.$$

This reaction is used on the large scale for the economic production of chlorine, and is known as Deacon's process. It is employed in the manufacture of bleaching powder (see p. 185).

Properties.—Chlorine is a transparent gas of a greenish-yellow colour, and possessing a most disagreeable and powerfully suffocating smell, which when the gas is present in small quantity only, resembles that of seaweed, but in large quantities produces violent irritation in the nose, mouth, and throat, giving rise to coughing and inflammation of the mucous membranes. If inhaled in the pure state it causes death. 1 litre of chlorine weighs $0.0899 \times 35.2 = 3.1645$ grms. Under a pressure of six atmospheres at $0°$, or when exposed to a temperature of $-34°$ at the ordinary atmospheric pressure, chlorine is condensed to a yellow liquid. At $-102°$ the liquid solidifies to a yellow crystalline mass.

Chlorine is soluble in water, to which it imparts its peculiar properties; one volume of water dissolves two volumes of chlorine, the solution is known as chlorine water and is used in the laboratory for various purposes. As chlorine also combines with mercury, it cannot be collected either over that metal or over water, but may easily be obtained by downward displacement (Fig. 81), as it is two and a half times as heavy as air.

Combustions in Chlorine

EXPT. 90.—Chlorine combines energetically with hydrogen, and if we lower a jet of burning hydrogen into a jar of chlorine, the flame continues to burn, but instead of gaseous water being the product of combustion, dense fumes of hydrochloric acid are produced. The presence of hydrochloric acid may be shown by holding a piece of moistened blue litmus paper in the fumes which are given off. It is immediately turned red.

The following experiments show the great power chlorine possesses, not only of combining with free hydrogen but with hydrogen in a state of combination.

EXPT. 91.—When a piece of filter paper moistened with turpentine, $C_{10}H_{16}$, is plunged into chlorine gas, so much heat is evolved in the combination of the chlorine with the hydrogen, that some of the turpentine takes fire, clouds of soot and fumes of hydrochloric acid being evolved.

EXPT. 92.—Another experiment is to plunge a lighted taper into a jar of chlorine; the taper continues to burn but with a smoky dull red flame which emits dense fumes of hydrochloric acid as well as a cloud of black soot. This is because the chlorine combines with the hydrogen of the wax and liberates the carbon.

EXPT. 93.—Moist chlorine also combines directly with metals, sometimes with evolution of light and heat. Thus if a few leaves of Dutch metal (copper in thin leaves) are placed in a round-bottomed flask furnished with a glass stopcock, and the flask be then exhausted of air, it will be found on opening the stopcock and admitting chlorine that the copper leaf will take fire and burn with the evolution of dense yellow fumes of copper chloride ($CuCl_2$).

EXPT. 94.—Similarly, if finely-powdered antimony be thrown into the gas a shower of sparks accompanies the formation of antimony chloride ($SbCl_3$).

EXPT. 95.—If sodium be melted in a deflagrating spoon and plunged into the moist gas, it takes fire, burning brightly, with the formation of sodium chloride ($NaCl$).

EXPT. 96.—A small piece of phosphorus placed in a deflagrating spoon, and plunged into chlorine, first melts and soon bursts into flame, with formation of the chlorides of phosphorus (PCl_3 and PCl_5).

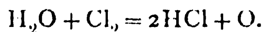
Chlorine also abstracts the hydrogen from sulphuretted hydrogen, H_2S, olefiant gas, C_2H_4, water, H_2O, and other hydrogen compounds.



$$H_2S + Cl_2 = 2HCl + S,$$



$$C_2H_4 + Cl_4 = 4HCl + C_2.$$



$$H_2O + Cl_2 = 2HCl + O.$$

Bleaching Action of Chlorine

We have seen above that chlorine has the power of decomposing water with liberation of oxygen. Chlorine water when exposed to sunlight soon loses its yellow colour, and hydrochloric acid is formed in the solution. At the moment of liberation of the oxygen, that gas has remarkably active bleaching powers ; thus if a piece of turkey red calico be dipped in chlorine water, the part immersed is soon decolorised. The oxygen which thus oxidises the colouring matter is said at the moment of its liberation to be in the *nascent state*, and this difference is probably due to its being in its free *atomic* condition, whilst in ordinary oxygen the free atoms have united to form the less active *molecules.*

$$\text{(Nascent oxygen) } 2O = O_2 \text{ (Ordinary free oxygen).}$$

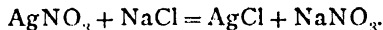
This view is confirmed by the fact that dry chlorine does not possess bleaching power, and a piece of turkey red cloth may be kept in the dry gas without losing its colour, whilst if moisture be afterwards admitted the colour quickly disappears.

Test for Chlorine.—Chlorine may be recognised by its characteristic smell, and by the fact that it colours iodised starch paper blue owing to the liberation of iodine.



$$KI + Cl = KCl + I.$$

It may also be recognised by its bleaching action and by its characteristic yellow colour. With silver nitrate, chlorine and all the soluble chlorides produce a white precipitate of silver chloride, which is insoluble in nitric acid but soluble in ammonia.



$$AgNO_3 + NaCl = AgCl + NaNO_3.$$

CHLORINE AND HYDROGEN

Hydrochloric Acid (Muriatic Acid)

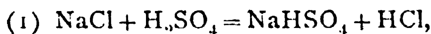
FORMULA HCl. MOLECULAR WEIGHT 36.2. DENSITY 18.1

Only one compound of chlorine and hydrogen is known, namely HCl. Glauber originally obtained this acid by the

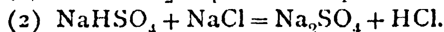
action of sulphuric acid on common salt about the year 1648. Priestley first obtained the gas itself by collecting it over mercury in the pneumatic trough. Before that time it was only known in solution, it being excessively soluble in water. But it was not until 1810 that Sir Humphry Davy proved it to be composed of hydrogen and chlorine only.

Occurrence.—The gas is not found free in nature except in small quantities in the gases evolved from certain active volcanoes. The occurrence of its salts has already been mentioned under chlorine (see also The Chlorides, p. 184).

Preparation.—(1) Hydrochloric acid is usually prepared by the action of concentrated sulphuric acid on common salt. The reaction takes place in two stages, in the first of which one molecule of each substance reacts on the other, thus—



$$(1)\ NaCl + H_2SO_4 = NaHSO_4 + HCl,$$



$$(2)\ NaHSO_4 + NaCl = Na_2SO_4 + HCl.$$

In the second reaction, the sodium hydrogen sulphate, or bisulphate of soda, decomposes another molecule of salt with

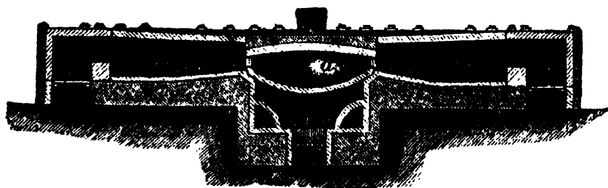


Fig. 82.

formation of another molecule of hydrochloric acid. For the second reaction a higher temperature is required.

EXPT. 97.—The apparatus used is exactly like that used for chlorine, and the method of preparation the same, hydrochloric acid gas being collected by downward displacement.

(2) Hydrochloric acid may also be produced by the direct combination of its elements, but this is not a convenient way of preparing it. To show the combination, a small jar of hydrogen is inverted over a similar jar of chlorine *in the dark*; after allowing the gases to mix, a lighted taper brought to the mouth of the jar will cause their instant combination, which is

accompanied by an explosion (see also explosive combination of chlorine and hydrogen, p. 181).

Manufacture of Hydrochloric Acid.—Hydrochloric acid is prepared on a very large scale as one of the bye-products in the manufacture of soda-ash (alkali) or carbonate of soda. In the alkali works 10 cwt. of salt is placed in a large iron pan *a* (Fig. 82), heated by a fire *b* placed underneath, and covered by

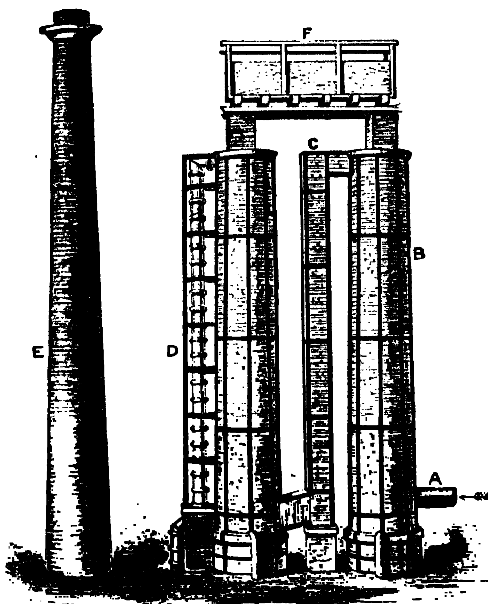
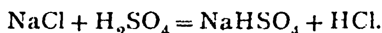


Fig. 83.

a dome or arch of brickwork. Upon this salt about an equal weight of sulphuric acid (sp. gr. 1.7) is run. Hydrochloric acid gas is then rapidly given off and led from the furnace by means of glazed stoneware pipes to high towers (shown in Fig. 83) built of bricks, or Yorkshire flag, soaked in tar and clamped together and filled with bricks or coke. Down the interior of the towers a stream of water is allowed to trickle from a cistern (F) placed on the top. The hot gas from the furnace is drawn off by the draught of the chimney

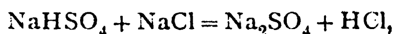
(E), and passes at (A) into the tower (B), where the greater part is absorbed; then the undissolved gas passes down the pipe (C) into the "exhaust" tower, where, in ascending, it again meets with a stream of water, and thus every trace of hydrochloric acid gas is absorbed. Formerly, the escape of this acid gas from alkali works was a great source of nuisance and damage to neighbouring property. Now, under careful inspection, the condensation of the acid is so perfect that no perceptible injury is effected, whilst the manufacturers save a valuable product which was at one time allowed to escape into the air.

In the pan *a* the first reaction takes place, in which the acid salt is formed, thus—



$$NaCl + H_2SO_4 = NaHSO_4 + HCl.$$

When this has taken place, the mass is raked on to the hearths of the reverberatory furnaces *dd*, and heated more strongly by the fires *cc*, when the further reaction is completed, viz.



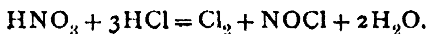
$$NaHSO_4 + NaCl = Na_2SO_4 + HCl,$$

and thus salt-cake or sodium sulphate, Na_2SO_4, is produced, and the whole of the hydrochloric acid given off.

Properties.—Hydrochloric acid is a colourless gas possessing an acrid choking smell. It can be condensed to a colourless liquid at -4, under a pressure of 25 atmospheres. The gas fumes strongly in the air, combining with the aqueous vapour there present. It is excessively soluble in water, one volume of water at 0° dissolving 503 vols. of the gas at NTP. The gas is heavier than air, and may be collected by downward displacement. Like all acids it turns blue litmus red.

The aqueous acid dissolves iron, zinc, magnesium, and other metals, with the formation of their chlorides and liberation of hydrogen.

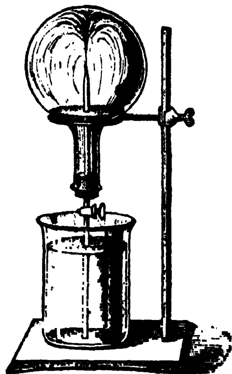
Aqua Regia.—A mixture of hydrochloric and nitric acids is known as *aqua regia*, because it dissolves the noble metals gold and platinum, the chlorides of these metals being formed. This is due to the liberation of chlorine and nitrosyl chloride, NOCl, during their mutual decomposition thus—



$$HNO_3 + 3HCl = Cl_2 + NOCl + 2H_2O.$$

Experiments with Hydrochloric Acid Gas

EXPT. 98.—If a well-covered jar of the gas be inverted over water in the pneumatic trough, and the cover slipped off, the water rushes up and fills the jar owing to the great solubility of the gas.


Fig. 84.

EXPT. 99.—The solubility of the gas, and also its acid nature, may be demonstrated by repeating Expt. 84, collecting the gas this time, however, by downward displacement, and using blue litmus solution, which is turned red on coming in contact with the gas (Fig. 84), showing that its reaction is acid.

EXPT. 100.—If the gas be led into a bottle half filled with water (Fig. 85), it will be seen that no bubble escapes, until the liquid becomes nearly saturated, the whole being absorbed by the water, giving rise to the aqueous acid. It is this aqueous solution which is commonly known as hydrochloric acid or muriatic acid, or sometimes as spirits of salt. This compound is a very powerful acid, and is much used in the arts.


Fig. 85.

Determination of Composition of Hydrochloric Acid

EXPT. 101. **Electrolysis of the Acid.**—The strong aqueous acid is decomposed into its elements, hydrogen and chlorine, by the electric current, but for this purpose platinum electrodes cannot be used as they were in the case of water, as chlorine rapidly attacks this metal. Carbon electrodes are therefore used for the decomposition. Fig. 86 shows the apparatus used for the electrolysis of hydrochloric acid. This experiment must be made in a very dim daylight or better in gaslight, as in bright sunlight

or even good daylight the mixed gases immediately combine with explosive violence.

To ascertain the composition of the gases which are evolved by the electrolysis of the acid, it is necessary to allow the decomposition to go on for some time before collecting them, as the chlorine is soluble in the liquid. After a steady evolution of the gas has continued for some time, the liquid becomes saturated with the gas, and no further absorption takes place. The mixed gases may then be collected for the purpose of ascertaining their composition.

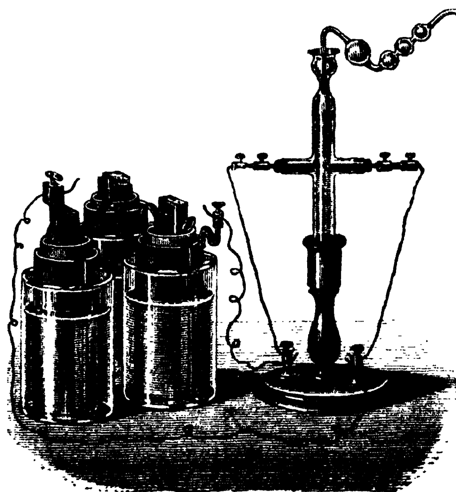


Fig. 86.

For this object the mixed gases are allowed to pass through thin bulb tubes (Fig. 87), and after the gases have been passing long enough to ensure that all the air is driven out from the bulbs, they are very carefully sealed before the blow-pipe, and the sealed bulbs preserved for use in a dark box.

EXPT. 102. **Action of the mixed Gases on Potassium Iodide.**—The capillary end of one of the bulb tubes is broken under mercury. It is seen that the bulb is full of the mixed gases and the mercury does not enter. Now, a solution of potassium iodide is placed on the top of the mercury, and the bulb tube raised so that a little of the solution enters. Iodine is now liberated by the chlorine, which is soon entirely absorbed, when it is seen that *half the original volume of gas remains*, the iodine having dissolved in the liquid (Fig. 88). On



Fig. 87.

depressing the bulb in water and breaking the other end of the tube it will be found that the remaining gas takes fire and burns with the characteristic flame of hydrogen. The mixed gas then consists—

(1) Of 1 volume of chlorine which is absorbed by the potassium iodide, the solid iodine dissolving in the liquid.



$$KI + Cl = KCl + I.$$

(2) Of 1 volume of hydrogen which remains and which may be burnt, giving the flame of burning hydrogen.

EXPT. 103. **Slow Combination of the mixed Gases in diffused Daylight.**—If another bulb be taken from the dark box in which they must be kept, and exposed first to a dim, and afterwards gradually to a stronger daylight, the yellow colour of the chlorine will be noticed slowly to disappear, after which the bulb may be exposed to strong daylight so as to complete the combination of the chlorine and hydrogen. If now the capillary tube of the bulb be broken under mercury, no change in the volume of the gas can be noticed, for no gas escapes and no mercury enters the bulb. If water be next poured on the surface of the mercury, and the end of the tube raised into it, the hydrochloric gas will be completely absorbed, and the water will entirely fill the bulb, showing that *equal volumes of hydrogen and chlorine combine together without change of volume* to form hydrochloric acid gas.

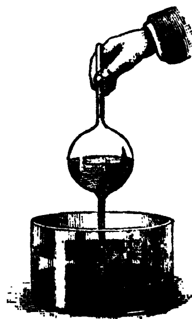
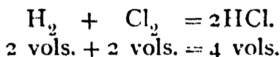


Fig. 88.



$$\begin{array}{ccccc} H_2 & + & Cl_2 & = & 2HCl. \\ 2 \text{ vols.} & + & 2 \text{ vols.} & = & 4 \text{ vols.} \end{array}$$

EXPT. 104. **Explosive Combination in bright Daylight.**—If a bulb filled with the mixed gases be taken from its dark box and exposed to bright daylight, immediate combination takes place throughout the mass, and so much heat is evolved, and the gas is thereby so greatly and suddenly expanded, that the bulb explodes and is shattered to fine dust.

EXPT. 105. **Explosion in the Light from burning**

Magnesium.—A convenient manner of showing the explosive combination of the two gases is exhibited in Fig. 89. The bulb is exposed to the light from burning magnesium, the face and hand being protected by a sheet of plate glass. This light is rich in chemically active rays, and causes the combination just as daylight does.

EXPT. 106. **Action of Hydrochloric Acid on Sodium Amalgam.**—Another experiment showing that hydrochloric acid gas contains half its volume of hydrogen may be made as follows. Into the open limb of the U tube (Fig. 90) mercury

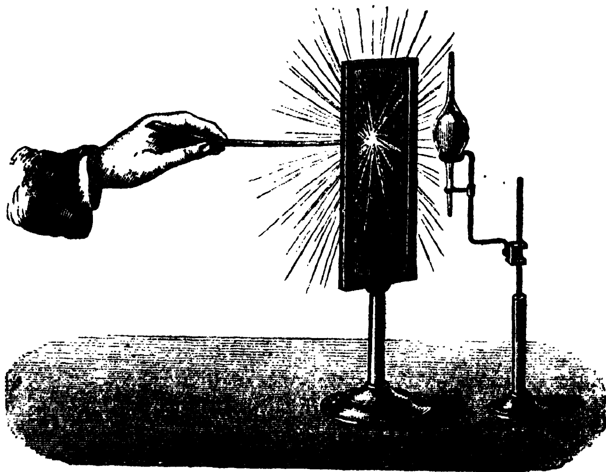


Fig. 89.

is poured until both limbs are full, the air being driven out of the left-hand limb through the open stopcock; the stopcock is now connected with a tube delivering pure and dry hydrochloric acid gas. The pinch-cock at the bottom of the U tube is now opened, so as to allow mercury to flow out, when the pure gas enters and fills the left-hand tube. After adjusting the level of mercury to the same height in both tubes, so that the gas fills the tube to the second mark (Fig. 90), sodium amalgam *

* Made by pressing, by means of a pestle, several small pieces of clean-cut sodium, one by one, under the surface of a few ounces of mercury contained in a porcelain mortar.

is poured into the open limb of the U tube so as to fill it completely. The open end of the tube is now closed by the thumb, and it is inclined and shaken so that the gas comes into intimate contact with the sodium amalgam. The gas is now again transferred to the closed limb, and the thumb removed from the open end, when a great diminution in the volume of the gas will be noticed. On adjusting the level of mercury to the same height in both tubes, it will be seen that the gas occupies just half the original volume (Fig. 91), whilst if mercury be poured into the open limb so as to fill it, the gas may be ignited on opening the stopcock, and seen to burn

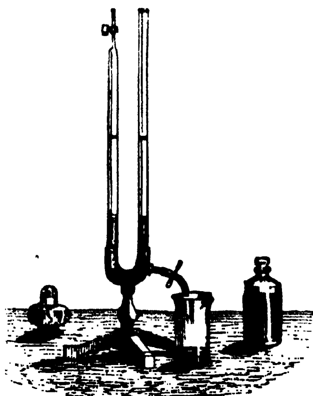


Fig. 90.

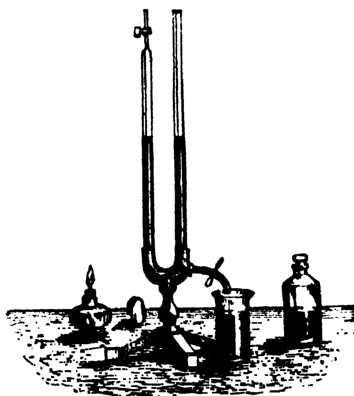
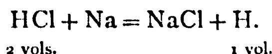


Fig. 91.

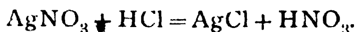
with the characteristic flame of hydrogen. The sodium of the amalgam has combined with the chlorine and liberated hydrogen which occupies half the volume of the hydrochloric acid, as is shown in the following equation,



$$\underset{\text{2 vols.}}{HCl} + Na = NaCl + \underset{\text{1 vol.}}{H}.$$

Test for Hydrochloric Acid.—Hydrochloric acid may be recognised by the fact that when heated with manganese dioxide chlorine is evolved, which may be recognised by its own characteristic tests. With silver nitrate solution, $AgNO_3$, all soluble chlorides as well as the acid form a curdy white

precipitate of AgCl insoluble in nitric acid but soluble in ammonia.



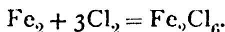
$$AgNO_3 + HCl = AgCl + HNO_3.$$

The Chlorides

Occurrence.—The metallic salts of hydrochloric acid are called chlorides. They occur plentifully in nature; common salt and rock salt, and also sylvine have already been mentioned. Potassium chloride also occurs as a double chloride of that metal and magnesium in the Stassfurt deposits and is called Carnallite, $KCl . MgCl_2 . 6H_2O$. Silver chloride, AgCl, occurs as horn silver, whilst ferric chloride is found in the craters of active volcanoes. The chlorides of the alkali metals sodium and potassium occur as essential constituents of the bodies of animals and plants.

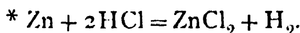
Preparation.—Chlorides may be formed either—

(1) By the direct combination of the metals with chlorine.



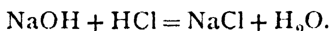
$$Fe_2 + 3Cl_2 = Fe_2Cl_6.$$

(2) The replacement of the hydrogen in hydrochloric acid by the metals either by dissolving the metal in an aqueous solution of the acid or by passing hydrochloric acid gas over the heated metal.



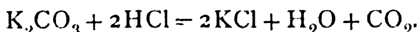
$$* Zn + 2HCl = ZnCl_2 + H_2.$$

(3) By the combination of basic oxides and hydroxides with hydrochloric acid.



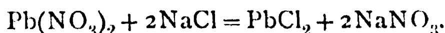
$$NaOH + HCl = NaCl + H_2O.$$

(4) By the decomposition of carbonates by the acid.



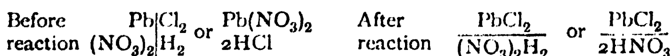
$$K_2CO_3 + 2HCl = 2KCl + H_2O + CO_2.$$

(5) By the double decomposition of two salts which together produce an insoluble or difficultly-soluble chloride.



$$Pb(NO_3)_2 + 2NaCl = PbCl_2 + 2NaNO_3.$$

This reaction is a type of an important class of reactions which are termed "*double decompositions.*"



Before reaction $\begin{array}{c|c} Pb & Cl_2 \\ (NO_3)_2 & H_2 \end{array}$ or $\begin{array}{l} Pb(NO_3)_2 \\ 2HCl \end{array}$ After reaction $\dfrac{PbCl_2}{(NO_3)_2H_2}$ or $\dfrac{PbCl_2}{2HNO_3}$

* Other metals such as Fe, Mg, Cd, Sn, Al, Ni, Co, etc. dissolve in hydrochloric acid with evolution of hydrogen, forming chlorides.

In these reactions both salts are mutually decomposed, and they may be considered as two couples, viz. the acid and basic parts of each, which change partners, the basic part of one combining with the acid part of the other, and *vice versâ*.

Separation of the Chlorides in Analysis

When hydrochloric acid or a soluble chloride such as sodium or ammonium chloride is added to a liquid containing a large number of metallic salts in solution, a double decomposition takes place (as shown in 5, p. 184), causing the precipitation of the insoluble chlorides of silver, mercury (mercur*ous* chloride), and lead,



$$AgCl \qquad HgCl \qquad PbCl_2.$$

These three metals are therefore classed together as Group I. in qualitative analysis. The precipitated chlorides may be filtered from the solution containing the remaining metals, whose chlorides are soluble. Groups II. and III. will be mentioned under "The Sulphides" (p. 197).

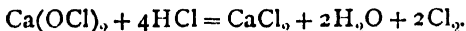
Bleaching Powder

When chlorine gas is passed over slaked lime, $Ca(OH)_2$, it is absorbed, and bleaching powder is produced, which is considered to be a mixture of two compounds, viz. calcium chloride, $CaCl_2$, and calcium hypochlorite, $Ca(OCl)_2$, corresponding to hypochlorous acid, $HClO$. The formation of bleaching powder may therefore be expressed as follows—



$$2Ca(OH)_2 + 2Cl_2 = CaCl_2 + Ca(OCl)_2 + 2H_2O.$$

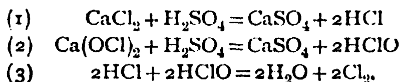
It is to the presence of the hypochlorite that bleaching powder owes its bleaching properties. For this compound is decomposed by hydrochloric acid, with liberation of chlorine,



$$Ca(OCl)_2 + 4HCl = CaCl_2 + 2H_2O + 2Cl_2.$$

With sulphuric acid the reaction is rather different, although the result is the same. The sulphuric acid liberates the hydro-

chloric and hypochlorous acids from their salts, and the free acids mutually decompose with liberation of chlorine and water, thus—



(1) $CaCl_2 + H_2SO_4 = CaSO_4 + 2HCl$
(2) $Ca(OCl)_2 + H_2SO_4 = CaSO_4 + 2HClO$
(3) $2HCl + 2HClO = 2H_2O + 2Cl_2$.

What we have learnt

In the eighteenth Lesson we have learnt the various methods of preparing chlorine and hydrochloric acid, and their most important properties. We have seen that chlorine is a heavy, yellow, poisonous gas which dissolves in half its bulk of water to form chlorine water. It combines directly with metals, bleaches organic colouring matters by an oxidising reaction in which water is decomposed and nascent oxygen liberated. Chlorine has a great affinity for hydrogen, and is able to abstract that element from many compounds containing it, such as H_2O, H_2S, C_2H_4, turpentine, etc. Equal volumes of chlorine and hydrogen form a mixture which only requires to be brought into strong daylight in order to explode.

The composition of hydrochloric acid has been exhibited by various experiments, the mixture of gases evolved on the electrolysis of the aqueous acid being shown to consist of equal volumes of chlorine and hydrogen. The separation of chlorides as the first group in the qualitative analysis of solutions of metallic salts has been explained, as well as the various methods of preparing chlorides. By passing chlorine over slaked lime we obtain bleaching powder, which may be considered as a mixture of calcium chloride and calcium hypochlorite.

Exercises on Lesson XVIII

1. By what reactions may chlorine be prepared? Sketch the apparatus you would use, and give an account of the principal properties of chlorine.
2. What volume of chlorine can I get at NTP from 50 grams of manganese dioxide which is decomposed by an excess of hydrochloric acid?
3. Explain the bleaching action of chlorine.
4. How is hydrochloric acid manufactured on the large scale? Give equations for the reactions.
5. How would you ascertain the composition of hydrochloric acid?
6. By what reactions may chlorides be prepared?
7. Explain the term "double decomposition."
8. How are the metallic chlorides used in qualitative analysis?
9. What is aqua regia?
10. Give characteristic tests for chlorine, hydrochloric acid, and chlorides.
11. Explain the action of chlorine on (1) water, (2) sulphuretted hydrogen, and (3) potassium iodide.

LESSON XIX

SULPHUR, SULPHURETTED HYDROGEN, AND THE SULPHIDES

Sulphur

SYMBOL S. ATOMIC WEIGHT 31.8. VAPOUR DENSITY 31.8

Occurrence.—The ancients were acquainted with sulphur. It is found in the free or "native" state near active as well as extinct volcanoes. The common name of brimstone is derived from Brennestone, or burning-stone, indicating its combustibility. Sulphur is not only found in the free state, but it is also met with in metallic ores, which contain sulphur combined with metals to form *sulphides*. Sulphur also occurs combined with oxygen as well as with a metal to form *sulphates*, some of which occur in large quantities. Some of the more important sulphides amongst the metallic ores may be here mentioned: *e.g.* Galena, lead sulphide, PbS; Cinnabar, mercury sulphide, HgS; Iron pyrites, iron di-sulphide, FeS_2 (this, however, has no value as an iron ore, but as a sulphur ore); Zinc Blende, zinc sulphide, ZnS.

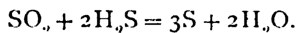
Among the commonly occurring sulphates are Gypsum, calcium sulphate, $CaSO_4.2H_2O$ (this, when heated, so as to drive off its 2 molecules of water of crystallisation, forms Plaster of Paris, $CaSO_4$); Heavy spar, barium sulphate, $BaSO_4$; Green Vitriol, ferrous sulphate, $FeSO_4.7H_2O$; Glauber salt, $Na_2SO_4.10H_2O$.

Sulphur is also found in nature in combination with hydrogen, as sulphuretted hydrogen, H_2S. This gas occurs dissolved

in the water of many mineral springs, such as that at Harrogate, imparting to it the well-known smell of rotten eggs.

Sulphur also occurs in a state of combination in many organic compounds, especially in animal substances, such as white of egg (albumen). When the albumen undergoes putrefaction, sulphuretted hydrogen is formed, and this is easily recognised by its peculiar and unpleasant smell.

Natural Deposition of Free Sulphur.—Volcanic gases contain sulphur in the form of sulphur dioxide, SO_2, as well as of sulphuretted hydrogen, H_2S; and when these two gases come together, they mutually decompose with deposition of sulphur, and it is probable that this is the explanation of the occurrence of free sulphur in volcanic districts. Their mutual decomposition is shown in the following equation—



$$SO_2 + 2H_2S = 3S + 2H_2O.$$

EXPT. 107.—This reaction can be readily shown by passing the two colourless gases into a large glass globe, when the deposit of solid yellow sulphur on the inside of the glass globe is clearly seen.

Purification of Crude Sulphur.—In order to obtain pure sulphur from the impure material found in quantity near Etna, in Sicily, the crude sulphur, which is found mixed with earthy and mineral matter, is placed in a kind of kiln built on sloping ground, so that, when fire is applied to the heap, a portion of the sulphur takes fire, and is burnt to sulphur dioxide, SO_2, whilst the remainder, and by far the larger quantity, is melted and runs out at an opening at the lower part of the kiln, where it flows into moulds, and is then sufficiently pure for exportation. In order further to purify it, this crude commercial sulphur, when it reaches this country, is refined by subjecting it to distillation, as shown in Fig. 92. The sulphur is placed in an iron boiler (G) and heated by a fire, whilst the vapour (D) from the boiling sulphur passes into a cool brick chamber (A), where it collects. If the temperature of this chamber is kept below 115°, at which point sulphur melts, the vapour quickly solidifies in the form of a fine yellow crystalline powder, known as flowers, or flour, of sulphur, just as the vapour of water, if cooled below 0°, the melting point of ice, solidifies in the form of crystalline

snow. When the heat of the chamber rises above 115° the sulphur vapour liquefies, and the liquid is then drawn off and cast into moulds, when it is known as roll sulphur or brimstone.

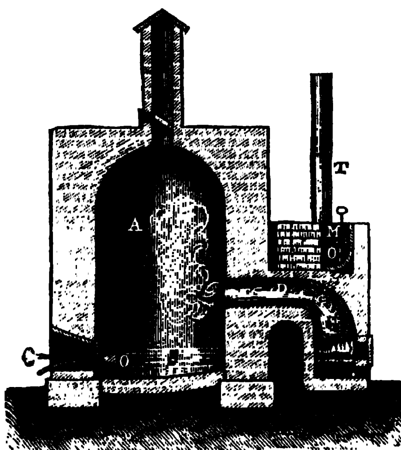
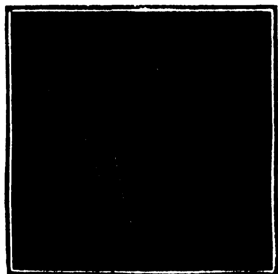


Fig. 92.

Sulphur is now also largely manufactured from the "waste" of the alkali works, and this method is gradually superseding the production of native or volcanic sulphur.

Allotropic Forms of Sulphur

Sulphur is remarkable as existing in several distinct *allotropic* forms. The first of these is that in which it occurs free in volcanic districts; it is there found crystallised in large transparent octahedrons belonging to the rhombic system shown in Fig. 93. The second form is also crystalline, and may be easily obtained as follows.


Fig. 93.

Expt. 108.—Let us place some pieces of brimstone in a clay crucible, and heat the crucible in the fire, or over a gas flame, until the sulphur is completely melted. We then remove the crucible, and allow it to cool, until a thin crust of solid sulphur is formed on the surface of the molten mass. Two holes are then pierced through the crust, and the liquid sulphur in the interior quickly poured out. On then breaking the crucible, or removing the whole of the top crust, a mass of transparent needle-shaped crystals is found to line the sides of the crucible. These

crystals are of a different shape from those occurring in nature, they belong to the monoclinic system of crystals. But if we allow this mass to remain in the crucible for twenty-four hours, it will then be seen that the crystals, which originally were transparent, have become opaque, and if they are then broken we notice that each needle-shaped crystal splits up into a number of small crystals, each of which, under a microscope, is seen to have the form of the first modification. Hence, the first is the permanent, whilst the second is a less permanent form. These varieties differ not only in crystalline form but in certain other respects; thus the specific gravity of the crystals of native sulphur is 2.05, whilst that of the crystals obtained by quickly cooling melted sulphur is 1.96. Moreover, the first modification melts at 114°.5, whereas the melting point of the second is 120°.

EXPT. 109.—That sulphur exists in a third allotropic condition can be easily shown. For this purpose we melt some sulphur in a flask, and gradually heat it further, when the pale yellow mobile liquid changes to a dark red viscid mass, until, when the temperature reaches 220°, the colour of the liquid is almost black. If we now pour out this thick liquid in a thin stream into cold water, the sulphur forms a soft sticky mass, something like caoutchouc, called *plastic sulphur*, because it can be drawn out into strings. Soon, however, it again assumes the yellow colour and brittle character of ordinary sulphur.

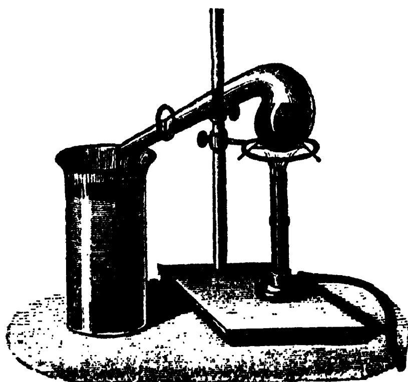


Fig. 94.

Fig. 94 shows the formation of plastic sulphur from the distilled sulphur which has condensed in a molten condition in the hot neck of the retort.

Properties.—Sulphur is a yellow solid body, which when heated to 440° in a retort begins to boil, giving off a red-

coloured vapour, which condenses in the neck of the retort, and sulphur may thus be purified on a small scale.

When sulphur is heated in the air, it takes fire and burns with a blue lambent flame; when burnt in oxygen (see Expt. 36) the combustion proceeds more quickly, and the light and heat evolved in a given time are greater. In both cases the compound formed is sulphur dioxide, SO_2, a colourless gas, sometimes called sulphurous acid gas, possessing the peculiar and well-known suffocating smell of burning sulphur.

Sulphur does not dissolve in water; it does so slightly in alcohol, and very easily in carbon disulphide, CS_2, from which solution it crystallises in the same form as native sulphur.

Sulphur combines with Metals to form Sulphides

EXPT. 110.—Instead of taking sulphur and iron filings as we did in Expt. 13, let us heat a mixture of flour of sulphur and finely-divided metallic copper in a test-tube; the mass will soon be seen to become red-hot, and, after cooling, the tube is found to contain a black mass of copper sulphide, CuS.

EXPT. 111.—Another way of showing this same combination is to boil some sulphur in a flask, and then to lower a coil of copper wire into the dark vapour. The copper soon becomes red-hot, and the molten sulphide produced drops to the bottom of the flask.

Tests for Sulphur

(1) Free sulphur may be recognised by the peculiar smell observed on burning it.

(2) A more delicate test for sulphur, whether in the free state or in a state of combination, is by heating the substance with concentrated nitric acid, which oxidises the sulphur to sulphuric acid. This may be recognised in the solution by adding barium chloride, $BaCl_2$, which produces a heavy white precipitate of barium sulphate, $BaSO_4$. When substances are present (such, for example, as barium carbonate) which render the sulphuric acid insoluble, a different method must be used (see "The Sulphates," p. 213). Further

tests for sulphur, when present as sulphides, sulphites, or sulphates, will be mentioned under their respective headings.

Sulphur resembles Oxygen in its power of Combination

We know (see p. 79) that carbon burns in the air, or in oxygen, to form carbon dioxide, CO_2; now, although carbon does not burn in the same way in sulphur vapour, yet, if we pass this vapour over red-hot charcoal, the charcoal gradually disappears, and we find that a colourless volatile liquid is formed by the union of the two elements. This liquid is carbon disulphide, CS_2, corresponding in composition to CO_2. So, too, H_2S, sulphuretted hydrogen, corresponds to H_2O, water, whilst the sulphides of the metals correspond to the oxides. This analogy is well seen in the following list of some compounds of oxygen in the upper line, and of the corresponding sulphur compounds in the lower—

H_2O	CO_2	P_2O_5	K_2O	KHO	CaO	PbO	HgO	FeO
H_2S	CS_2	P_2S_5	K_2S	KHS	CaS	PbS	HgS	FeS

Compounds of Sulphur and Hydrogen

Just as oxygen forms two compounds with hydrogen, viz. H_2O and H_2O_2, so sulphur forms two compounds, having a similar composition, viz. H_2S, sulphuretted hydrogen or hydrogen sulphide, and H_2S_2, hydrogen disulphide. The first of these is a gas at ordinary temperatures, the second is a liquid.

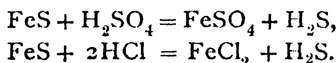
Sulphuretted Hydrogen,
Hydrogen Sulphide, or Hydrosulphuric Acid

FORMULA H_2S. MOLECULAR WEIGHT 33.8. DENSITY 16.9

Occurrence.—It has already been stated that this compound is found dissolved in certain mineral waters, and also that it exists in volcanic emanations, and is produced by the

putrefaction of animal matters, such as albumen, which contain sulphur in combination. It also occurs in the manufacture of coal gas, and has to be removed before the gas is sent out for consumption.

Preparation.—(1) Sulphuretted hydrogen is best prepared by acting with an acid on a metallic sulphide, and for this purpose sulphide of iron, FeS (obtained by heating together sulphur and iron filings, see Expt. 13), is generally employed. This sulphide is acted upon by dilute sulphuric or hydrochloric acid, when the gas is rapidly evolved, sulphate or chloride of iron being formed, according to the kind of acid used. The reactions are as follows:—



$$FeS + H_2SO_4 = FeSO_4 + H_2S,$$
$$FeS + 2HCl = FeCl_2 + H_2S.$$

EXPT. 112.—The apparatus shown in Fig. 95 serves to prepare and purify the gas; the iron sulphide is placed in the flask provided with a thistle funnel, and dilute acid added; the gas evolved bubbles through the water contained in the second flask, and is thus purified from any acid which might pass or spurt over. The gas delivery tube, instead of being bent at right angles as in Fig. 95, may be so arranged as to pass into a pneumatic trough, if it is desired to collect jars full of the gas. The water in the trough and jars should, however, be warm, as water dissolves three times its volume of the gas at ordinary temperatures, but the solubility decreases as the temperature of the water rises. It is advisable for laboratory use, as we shall see directly, to possess a means of obtaining either a small or large quantity of this gas at will. This is accomplished by using a Kipps's apparatus shown in Fig. 96. It consists of three glass globes, the two lower ones

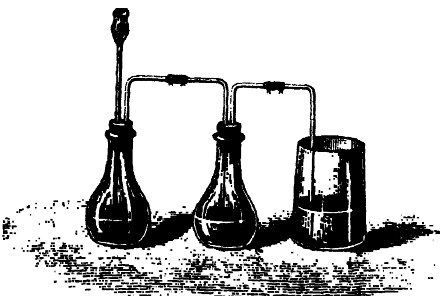


Fig. 95.

(*a*) and (*b*) being connected by a narrow neck, whilst the tubulus of the third globe (*c*) passes air-tight through the neck of (*b*). Iron sulphide in lumps is placed in globe (*b*), and dilute sulphuric acid poured in through the funnel tube until the globe (*a*) is filled, and some of the acid rises on to the sulphide of iron. Sulphuretted hydrogen gas is then evolved, passing out by the stopcock (*e*) into the wash bottle. When it is wished to stop the current of gas the cock (*e*) is closed, and in consequence of the gas accumulating in the globe (*b*), the pressure inside this globe increases, and thus forces out the acid up the tubulus into the upper globe (*c*), then the evolution of gas ceases and the whole apparatus may be allowed to stand until the gas is again required.

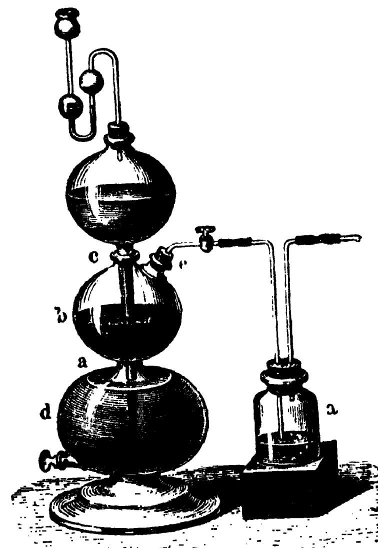
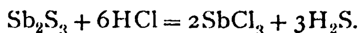


Fig. 96.

Why the Gas thus obtained is not Pure.—If we wish to obtain perfectly pure sulphuretted hydrogen, we must use natural sulphide of antimony, Sb_2S_3, instead of artificial sulphide of iron, because this latter always contains some particles of metallic iron, and these, when acted upon by an acid, dissolve with evolution of hydrogen gas, and this hydrogen cannot be readily separated from the sulphuretted hydrogen. On the other hand, antimony sulphide, being a pure compound, dissolves without evolution of any hydrogen. Thus



$$Sb_2S_3 + 6HCl = 2SbCl_3 + 3H_2S.$$

(2) Sulphuretted hydrogen is also formed in small quantities when hydrogen is passed through boiling sulphur.

Properties.—Sulphuretted hydrogen is a colourless invisible gas, which possesses a sweetish taste, and a very power-

ful and disagreeable smell, like that of rotten eggs. It is a poisonous gas, and, when inhaled in the pure state, it produces insensibility; and, if the inhalation be continued, it causes death. Hence experiments with this gas should be made in a draught chamber or in the open air.

EXPT. 113.—Collect two cylinders full of sulphuretted hydrogen in the pneumatic trough over hot water. Apply a lighted taper to the mouth of one cylinder, and observe that the gas burns with a blue lambent flame, the hydrogen burning to form water, and the sulphur partly burning to sulphur dioxide (SO_2), which can easily be recognised by its pungent smell, and partly being deposited as a yellow film on the sides of the jar.



$$H_2S + O = H_2O + S,$$



$$H_2S + 3O = H_2O + SO_2.$$

The flame of a lighted taper plunged into the second cylinder is seen to be extinguished, and can be re-ignited at the mouth where the sulphuretted hydrogen is burning.

Liquefaction of Sulphuretted Hydrogen.—Like all gases, this compound can be liquefied by cold or pressure, or both combined. If cooled to $-62°$ it condenses to a colourless liquid, which, if further cooled to $-85°$, freezes to an ice-like solid. So, too, if we expose the gas to a pressure of about 17 atmospheres, it likewise liquefies.

Tests for Sulphuretted Hydrogen and the Sulphides

(1) Sulphuretted hydrogen may be readily detected by its characteristic smell.

(2) A piece of filter paper, moistened with a solution of lead acetate, is stained black when brought in contact with this gas, owing to the formation of black lead sulphide, PbS.

(3) Sulphuretted hydrogen, or any soluble sulphide, gives a very characteristic purple colour to an alkaline solution of sodium nitroprusside.

(4) Sulphides are decomposed by hydrochloric acid, with liberation of sulphuretted hydrogen, which may be tested for by tests (1) and (2) above.

From test No. 2 it is easily understood why white-lead paint is soon turned black near gas-works, sewers, or other places where sulphuretted hydrogen is allowed to escape into the air.

The blackening of silver articles, and especially silver egg-spoons, is also due to the formation of black silver sulphide, Ag_2S.

Use of Sulphuretted Hydrogen in Analysis.—Sulphuretted hydrogen is largely used in analysis for the separation of the sulphides of the metals of Group II. which are insoluble in acids, and for the further separation of the metals of Group III. which are insoluble in alkaline and neutral solutions. For further details see "The Sulphides," p. 197.

Determination of Composition.—When strongly heated, this gas decomposes into sulphur and hydrogen, the sulphur being deposited in the solid form. For the purpose of determining the composition of sulphuretted hydrogen, we take a tube, having sealed through the glass a spiral of thin platinum wire, which can be heated white-hot by a current of electricity. Fill the tube with sulphuretted hydrogen up to a given mark, and place the tube over hot water. Then pass a current of electricity through the coil of wire, and observe that sulphur is deposited. After a time allow the whole to cool, and notice that the bulk of gas is unchanged. Now remove the tube and light the gas, which burns with the blue flame of hydrogen, without formation of sulphur dioxide, showing that all the sulphuretted hydrogen has been decomposed. What do we conclude from this? (1) That sulphuretted hydrogen contains its own volume of hydrogen; therefore, two volumes of the compound gas contain two volumes of hydrogen weighing 2. But by weighing the sulphuretted hydrogen gas, chemists have found that it is 16.9 times as heavy as hydrogen, or two volumes weigh 33.8, when the same volume of hydrogen weighs 2. If we now deduct this weight of hydrogen from 33.8, we have left 31.8 for the weight of the sulphur contained in two volumes of sulphuretted hydrogen, or the gas is composed of one atom of sulphur weighing 31.8, and two atoms of hydrogen weighing 2, and its formula is, therefore, H_2S.

The Sulphides

Occurrence.—Many sulphides occur in nature as metallic ores, and have already been mentioned under sulphur, *e.g.* Galena, Cinnabar, Zinc Blende, Iron Pyrites.

Separation of the Sulphides in Analysis

The filtrate which was obtained from the chlorides of Group I. of the metals (see p. 185) contains salts of the metals of all the succeeding groups. If sulphuretted hydrogen gas be passed through this solution, to which must be added free hydrochloric acid, a precipitate is formed, consisting of the sulphides of the metals of Group II., viz. mercury,‡ lead,† bismuth, copper, cadmium, antimony, arsenic, and tin; their formulæ are—



$$HgS, PbS, Bi_2S_3, CuS, CdS, Sb_2S_3, As_2S_3, SnS.$$

All these sulphides are insoluble in dilute hydrochloric acid. If they are filtered off, and the clear filtrate is made alkaline with ammonia so as to form ammonium sulphide with the free sulphuretted hydrogen dissolved in the liquid, a further precipitation of the sulphides of the metals of Group III. takes place, viz. sulphides of iron, aluminium, chromium, nickel, cobalt, manganese, and zinc—



$$FeS, Al_2S^*_3, Cr_2S^*_3, NiS, CoS, MnS, \text{ and } ZnS.$$

These sulphides are soluble in hydrochloric acid, and hence were not precipitated in Group II., when free acid was present. They are, however, insoluble in neutral or alkaline solutions, and may, therefore, be precipitated together by adding ammonium sulphide to their neutral or alkaline solutions, or by passing

‡ Mercury forms two series of salts, viz. the mercurous and mercuric salts corresponding to mercurous oxide, Hg_2O, and mercuric oxide, HgO, *e.g.* mercurous chloride (calomel), Hg_2Cl_2, insoluble in water; mercuric chloride (corrosive sublimate), $HgCl_2$, soluble in water.

† Lead chloride is slightly soluble in cold water, hence a little lead chloride remains dissolved in the filtrate from Group I. and gives rise to a precipitate of insoluble lead sulphide in Group II.

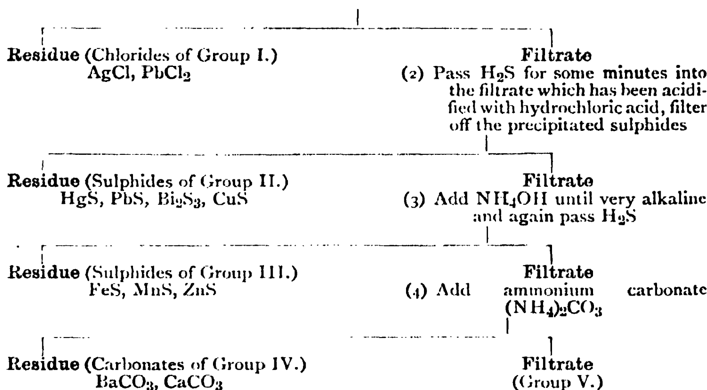
* The hydrated oxides of these two metals are in fact precipitated, as their sulphides are at once decomposed.

sulphuretted hydrogen through their solutions containing an excess of free ammonia. The filtrate from the sulphides of Group III. contains metals whose sulphides are soluble both in acid and in alkaline solutions, such as barium, strontium, calcium, magnesium, sodium, and potassium. The first three of these are separated from the rest by adding ammonium carbonate to the clear filtrate from Group III., when a precipitate of the carbonates of Group IV. is obtained, viz. $BaCO_3$, $SrCO_3$, $CaCO_3$. Group V. contains the metals magnesium, potassium, sodium, and ammonium.

Separation of Metals into Groups in Analysis

Let us make, for example, a mixture of the nitrates (all nitrates are soluble in water) of silver, lead, mercury (mercuric), bismuth, copper, iron, manganese, zinc, barium, and calcium.

(1) Add hydrochloric acid to the solution and filter off the precipitated chlorides.



In a similar manner the individual metals in all the groups may be tested for and separated from one another; but as it is not our purpose in this book to study these separations more fully, a work on Qualitative Analysis must be consulted for further information on this subject.

Hydrogen Disulphide, H_2S_2

This substance is an oily liquid obtained by pouring a solution of calcium disulphide into hydrochloric acid :—



$$CaS_2 + 2HCl = CaCl_2 + H_2S_2$$

This compound is not used in the arts, but it is interesting as having a composition corresponding to H_2O_2, and because, like this substance, it possesses bleaching properties. It easily decomposes into sulphuretted hydrogen and free sulphur.

What we have learnt

In our nineteenth Lesson we have learnt how sulphur is found in nature both in the free state and in metallic ores, as sulphides and sulphates. We have learnt the methods by which sulphur is purified, and also its principal properties. Sulphur exists in three allotropic modifications, and forms compounds with metals called sulphides which correspond in composition to the oxides. The occurrence and methods of preparing sulphuretted hydrogen as well as its properties, tests, and mode of determining its composition, have been considered. Its use as a *re-agent* in analysis, and also the method of separating the metals into groups have been described, and thus an idea has been obtained of the principles upon which qualitative analysis is founded.

Exercises on Lesson XIX

1. By what reaction is native sulphur formed in volcanic districts? Describe the various allotropic forms of sulphur.
2. Name some naturally occurring sulphides and sulphates, and give their chemical names and formulæ.
3. Explain the following reaction—$FeS + H_2SO_4 = FeSO_4 + H_2S$. If I want ten litres of sulphuretted hydrogen (NTP), how many grams of pure ferrous sulphide must I employ?
4. Explain precisely how the composition of sulphuretted hydrogen has been determined.
5. Give the tests for sulphur, sulphuretted hydrogen, and a sulphide.
6. Explain in detail how the metals contained in a mixture of metallic salts may be separated into groups.

LESSON XX

OXIDES AND OXY-ACIDS OF SULPHUR

SULPHUR DIOXIDE, SULPHUROUS ACID, AND THE SULPHITES. SULPHUR TRIOXIDE, SULPHURIC ACID, AND THE SULPHATES.

Sulphur Dioxide
Sulphurous Acid Gas or Sulphurous Anhydride

FORMULA SO_2. MOLECULAR WEIGHT 63.6. DENSITY 31.8

SULPHUR dioxide is a colourless suffocating gas, and is the compound to which burning sulphur owes its characteristic odour. The ancients knew that when sulphur burns, pungent smelling vapours are given off, and these fumes were then, as now, employed as a means of fumigation. Priestley, however, first prepared the pure gas in 1775. Its occurrence in volcanic gases has already been mentioned.

Preparation.—(1) For laboratory purposes this gas is prepared by the action of hot concentrated sulphuric acid upon copper turnings.



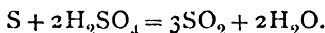
$$Cu + 2H_2SO_4 = CuSO_4 + 2H_2O + SO_2.$$

EXPT. 114.—The apparatus used is the same as for the preparation of chlorine or hydrochloric acid (Fig. 81). Copper turnings are placed in the flask so as to well cover the bottom. Cold concentrated sulphuric acid is then poured down the thistle funnel until the copper is covered. The flask

is then heated carefully on a sand-bath until the evolution of gas begins, when the heat must be moderated so as to keep the current of gas under control. Collect several jars of the gas in the draught chamber by downward displacement as it is very soluble in water, and is more than twice as heavy as air.

(2) On the large scale, sulphur dioxide is prepared by burning sulphur or iron pyrites, FeS_2, and immense volumes of the gas thus obtained are daily used in the manufacture of sulphuric acid (see p. 207).

(3) Pure sulphur dioxide may also be obtained by heating sulphur with concentrated sulphuric acid, the latter giving up a portion of its oxygen which oxidises the sulphur.



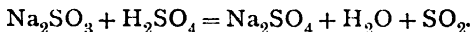
$$S + 2H_2SO_4 = 3SO_2 + 2H_2O.$$

(4) Charcoal is similarly oxidised to CO_2, whilst the sulphuric acid is reduced as before to sulphur dioxide.



$$C + 2H_2SO_4 = 2SO_2 + CO_2 + 2H_2O.$$

(5) The gas may also be obtained by the action of dilute sulphuric acid on sulphites (see p. 205).



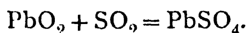
$$Na_2SO_3 + H_2SO_4 = Na_2SO_4 + H_2O + SO_2.$$

Experiments with Sulphur Dioxide

EXPT. 115.—Repeat Experiments 98 to 100 with this gas instead of hydrochloric acid, proceeding exactly as before, to show its very great solubility in water and its acid properties.

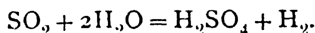
Properties.—Sulphur dioxide is a colourless gas possessing a very pungent suffocating odour which is well known as that given off by burning sulphur. It is 2.2 times as heavy as air and 31.8 times as heavy as hydrogen. It is very soluble in water, one volume at 0° absorbing nearly 80 volumes of the gas, whilst even at 20° nearly 40 volumes are dissolved, hence it cannot be collected over water. It can, however, be collected over mercury. It is a powerful antiseptic, and has been largely used in the preservation of meat, and is used for disinfecting purposes. It does not support the combustion of a taper.

Lead dioxide ignites when plunged into the gas, lead sulphate being produced.



$$PbO_2 + SO_2 = PbSO_4.$$

Sulphur dioxide (or sulphurous acid), like chlorine, possesses bleaching properties, but for another reason, *i.e.* because of its power of liberating nascent hydrogen from water, which *reduces* colouring matters to colourless compounds, whilst chlorine bleaches by an oxidising action. Sulphur dioxide is used for bleaching straw, silk, and woollen goods.



$$SO_2 + 2H_2O = H_2SO_4 + H_2.$$

Liquefaction of Sulphur Dioxide.—This compound is the most easily condensible of all the gases, for it may be

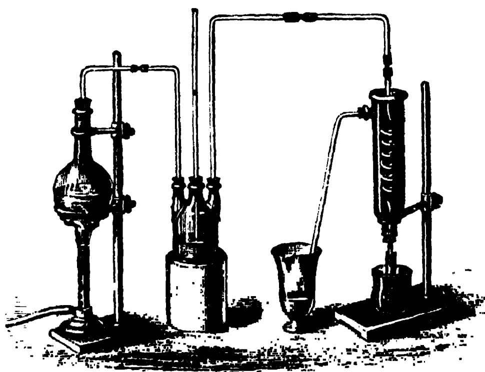


Fig. 97.

obtained in the liquid state at a temperature of $-10°$ or a pressure at $0°$ of only 1.53 atmospheres.

EXPT. 116.—To obtain the liquid the arrangement shown in Fig. 97 is employed. Sulphur dioxide is generated in the flask from a mixture of copper turnings and strong sulphuric acid, it is purified by passing through a small quantity of water contained in the wash-bottle, thence it passes into a glass worm-tube which is placed in a cylinder filled with a freezing mixture made by pounding up two parts of ice with one part of common salt (NaCl), by which a temperature of $-18°$ is

reached. The gas here condenses to a colourless liquid which may be collected in a small flask also plunged into some of the freezing mixture. Liquid sulphur dioxide boils at – 8°, and if cooled below – 75° it freezes to a transparent solid.

EXPT. 117.—Another simple experiment shows that sulphur dioxide gas can be liquefied at the ordinary temperature by pressure alone. For this purpose we take an ordinary strong glass tube closed and drawn out to a point at one end but open at the other. This is filled with the gas by displacement; and then a plunger, made of an iron rod to the end of which is fitted a greased india-rubber stopper which fits the bore of the glass, is inserted and forced down the tube. When this plunger has been forced down so that the gas occupies about one-fifth of its original volume, it will be seen that drops of liquid are formed which run down into the drawn-out end of the tube. If the plunger be now quickly withdrawn the liquid is seen to boil, and so much heat is absorbed by the vaporisation of the liquid that a portion of it freezes to a white solid.

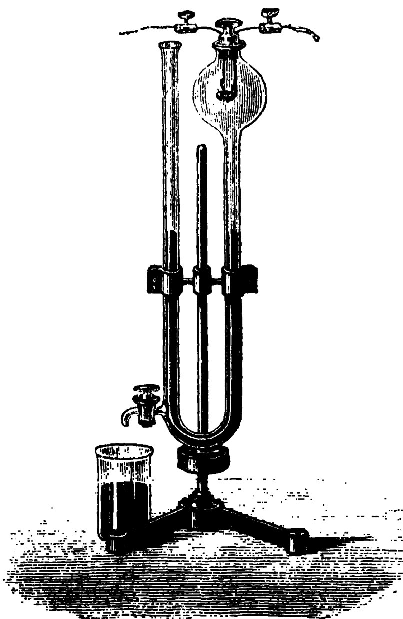


Fig. 98.

Determination of Composition of Sulphur Dioxide

EXPT. 118.—How do we ascertain that the formula SO_2 represents the composition of this gas? For this purpose the apparatus shown in Fig. 98 is used. The bulb is closed by a

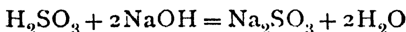
hollow stopper through which two stout copper wires are cemented; one of these ends in a small platinum spoon, the other in a thin piece of platinum wire which lies inside the spoon. A small piece of sulphur is placed over the thin wire in the spoon, and the bulb and tube having been filled with oxygen gas, and the stopper placed in position, and the level of mercury in the tubes observed, the sulphur is ignited by heating the wire by a current of electricity, care being taken to draw some mercury off by the tap so as to reduce the pressure of the gas and counteract the expansion due to the increase of temperature from the burning sulphur. As soon as the combustion is complete, the apparatus is allowed to cool, when it is found that the level of the mercury rises exactly to that which it occupied before the experiment, the mercury which had been allowed to flow out of the stopcock having been poured back through the open limb of the tube. What does this show? It shows that sulphur dioxide contains its own volume of oxygen. We know, however, from experiment that this gas is 31.8 times as heavy as hydrogen or two volumes weigh 63.6 when hydrogen weighs 2, but two volumes of oxygen weigh 31.8 or (15.9×2), therefore the weight of the sulphur in two volumes of this gas is 31.8 (one atom of sulphur) and that of the oxygen is also 31.8 (two atoms of oxygen); that is, sulphur dioxide is represented by the formula SO_2, and is made up of equal weights of sulphur and oxygen.

Sulphurous Acid, H_2SO_3

EXPT. 119.—If instead of passing the gas SO_2 into the coil tube shown in Fig. 97, we replace this coil by a straight tube and allow the gas to pass into a bottle of water, we shall notice that no bubble of gas reaches the surface of the water, it is all absorbed, one volume of water at the ordinary temperature absorbing about 50 volumes of the gas. The solution thus obtained retains the characteristic smell of the gas; it is an acid liquid, turning blue litmus paper red, and contains sulphurous acid, H_2SO_3, and only by prolonged boiling can all the SO_2 be driven out of solution. If water at 3° be saturated with the gas, and the solution allowed to stand, a crystalline hydrate of sulphurous acid is deposited.

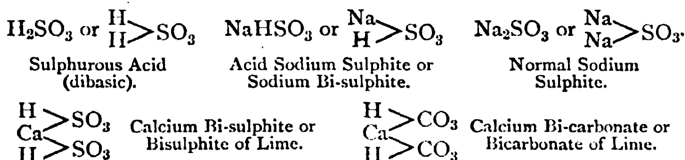
The Sulphites
Normal Sulphites, Acid Sulphites

If an alkali, such as caustic soda, be added to sulphurous acid, the acid reaction disappears and a crystalline salt termed a sulphite is formed thus—



$$H_2SO_3 + 2NaOH = Na_2SO_3 + 2H_2O$$

Sulphurous acid and caustic soda yield sodium sulphite and water. Sulphurous acid is the first example we have had of a *dibasic* acid; that is, it contains two atoms of hydrogen in the molecule, one or both of which may be replaced by a metal, so that two series of sulphites thus exist. In the first series only half the hydrogen is replaced, whilst in the second series all the hydrogen is replaced.



The bisulphites are largely used as antiseptics. The formula of calcium bisulphite may be represented as above, for calcium is a dyad metal, replacing two atoms of hydrogen, and one atom of calcium may be supposed to decompose two molecules of the acid in order to replace two atoms of hydrogen. These acid salts are, as their name implies, both acids and salts, for they are compounds containing hydrogen replaceable by metals, *i.e.* acids, and they are also acids in which hydrogen has been replaced by a metal, *i.e.* salts. Carbonic acid, H_2CO_3 (see p. 228), is likewise dibasic; its acid calcium salt may be represented as above. Both the normal and acid sulphites of sodium and potassium are used in photography, and bisulphite of calcium is used as a disinfectant and preservative.

Sulphur Trioxide, or Sulphuric Anhydride

FORMULA SO_3. MOLECULAR WEIGHT 79.5. VAPOUR DENSITY 39.75.

Preparation.—(1) Sulphur trioxide is a crystalline solid body, obtained by passing a mixture of perfectly dry sulphur

dioxide and oxygen through a tube containing heated platinum sponge or platinised asbestos.*



$$SO_2 + O = SO_3.$$

If the gases are passed over the platinum sponge when it is cold no combination takes place; but directly it is heated, dense white fumes of the trioxide are produced, and if these are passed into a perfectly dry receiver, cooled by a freezing mixture, the trioxide condenses in the form of beautiful long white silky needles. To obtain these, every portion of the apparatus must be perfectly dry, as the compound combines with water so readily, that a trace of it causes the crystals to deliquesce with formation of liquid sulphuric acid.

(2) Sulphur trioxide may also be prepared by the careful distillation of Nordhausen sulphuric acid or fuming oil of vitriol, which is concentrated sulphuric acid containing the trioxide in solution.

(3) Sulphuric anhydride may also be prepared by abstracting the elements of water from anhydrous sulphuric acid by means of phosphorus pentoxide.

Properties.—Sulphur trioxide is a crystalline solid, which melts at 14.8°, and boils at 46°. It absorbs moisture readily from the atmosphere, and evolves dense white fumes of sulphuric acid. It combines with water with a hissing sound, and with the evolution of a large amount of heat. It is an acid-forming oxide, and combines with the basic oxide, Baryta, BaO, with such force, that in the formation of the salt, $BaSO_4$, the mass becomes red-hot.

Determination of Composition

On passing the vapour of the trioxide through a red-hot tube it is decomposed into two volumes of SO_2, and one

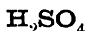
* Platinised asbestos is made by igniting asbestos fibres which have been covered with the yellow crystalline double chloride of platinum and ammonium, $PtCl_4 . 2(NH_4)Cl$. This decomposes on ignition, leaving behind metallic platinum in a finely-divided state. Platinum sponge is made by igniting the double chloride alone.

volume of oxygen, and since its vapour density is found to be 39.75, its formula must be SO_3.



$$\underset{}{SO_3} = \underset{\text{2 Vols.}}{SO_2} + \underset{\text{1 Vol.}}{O}.$$

Sulphuric Acid, Vitriolic Acid or Oil of Vitriol,

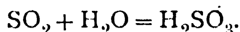


H_2SO_4

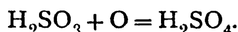
Sulphuric acid is the most important and most useful of all the acids, and by its means nearly all the other acids are prepared. It is manufactured on an enormous scale, nearly a million tons being annually manufactured in Great Britain, thus giving rise to a most important modern industry.

Manufacture of Sulphuric Acid

The manufacture of sulphuric acid on the large scale consists in allowing (1) sulphur dioxide; (2) steam; (3) air, and (4) a small amount of the fumes of nitric acid to pass together into a capacious chamber lined and floored entirely with sheet lead (Fig. 100). We may suppose, for simplicity, that the sulphur dioxide and steam unite to form sulphurous acid, which is afterwards oxidised to sulphuric acid by the oxygen of the air.



$$SO_2 + H_2O = H_2SO_3.$$

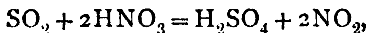


$$H_2SO_3 + O = H_2SO_4.$$

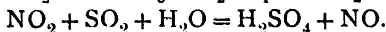
But, as a matter of fact, this oxidation only takes place very slowly indeed if atmospheric air alone be used, and here it is that the action of the nitric acid vapour, which is of the greatest interest, must be taken into account.

The vapour of nitric acid, made from Chili saltpetre, $NaNO_3$, and sulphuric acid (see p. 149) is passed continuously in small quantity into the flue, along which is passing the sulphur dioxide, obtained by burning either sulphur itself, or the sulphur contained in iron pyrites, FeS_2.

The nitric acid is at once reduced to nitrogen-peroxide, which in turn is further reduced to nitric oxide. Thus

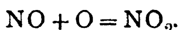


$$SO_2 + 2HNO_3 = H_2SO_4 + 2NO_2,$$



$$NO_2 + SO_2 + H_2O = H_2SO_4 + NO.$$

The nitric oxide, as we know, will at once absorb oxygen from the air, and be converted to the red fumes of the higher oxides, N_2O_3 and NO_2.



$$NO + O = NO_2.$$

This peroxide in turn reacts on more sulphur dioxide and steam, to form sulphuric acid, nitric oxide again being formed. In this manner the nitric oxide which is obtained by the reduction of the vapour of nitric acid acts as a *carrier of*

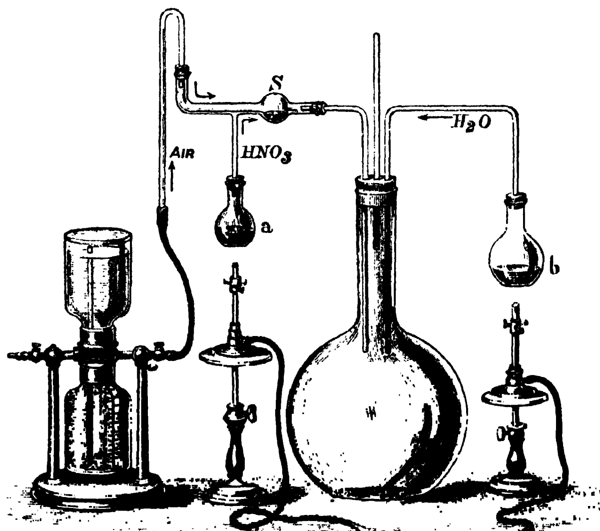
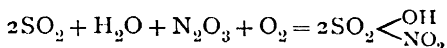


Fig. 99.

atmospheric oxygen, alternately abstracting it from the air, and then giving it up again for the oxidation of the sulphur dioxide; hence it is that a very small proportion of nitrous fumes will suffice to bring about an oxidation, by atmospheric oxygen, of very large volumes of sulphur dioxide, which atmospheric air alone would be quite powerless to effect.

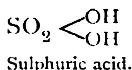
The reactions by which sulphuric acid is thus produced on a large scale may be illustrated by means of the apparatus shown in Fig. 99. Sulphur is heated in the bulb tube *S*,

and allowed to burn in a stream of air forced forward by a double aspirator. A mixture of nitre and sulphuric acid in *a* evolves nitric acid vapours which pass into the large flask along with the sulphur dioxide and air. Here the gases meet with steam from the boiling water in *b*, and they condense on the sides of the large flask as drops of sulphuric acid. By alternately increasing and diminishing the supply of sulphur dioxide, the disappearance and reappearance of the red nitrous fumes can be readily shown. If the flask into which the gases are passed is kept dry by keeping back the steam, white crystals, known as leaden chamber crystals, are formed, having the formula $HSO_3(NO_2)$.



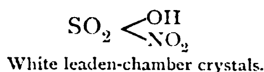
$$2SO_2 + H_2O + N_2O_3 + O_2 = 2SO_2<^{OH}_{NO_2}$$

We may suppose it to be sulphuric acid in which one of the hydroxyl groups (OH) is replaced by NO_2. Thus



$$SO_2 <^{OH}_{OH}$$

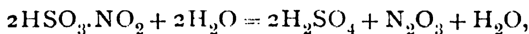
Sulphuric acid.



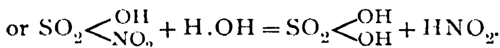
$$SO_2 <^{OH}_{NO_2}$$

White leaden-chamber crystals.

When steam is admitted the crystals dissolve with formation of sulphuric acid and red fumes of N_2O_3.



$$2HSO_3.NO_2 + 2H_2O = 2H_2SO_4 + N_2O_3 + H_2O,$$



$$\text{or } SO_2<^{OH}_{NO_2} + H.OH = SO_2<^{OH}_{OH} + HNO_2.$$

It is evident that in the manufacture of sulphuric acid on a large scale, it is of the utmost importance to adjust the due proportion of the various gases, viz. (1) sulphur dioxide, (2) air, (3) nitric fumes, and (4) steam, with great nicety. If too much steam be passed into the chambers, they become too hot, and the acid is, moreover, weakened. If the nitrous fumes are deficient, the oxidation of the sulphur dioxide does not take place properly. If too much air be admitted, the gases are unnecessarily diluted, and the reactions do not take place so readily.

The gases which pass into the leaden chambers (Fig. 100) are drawn through them by a powerful draught produced by the uprush of heated air in a tall chimney. Besides the residual nitro-

gen from the air, a certain amount of the nitrous fumes pass out with the nitrogen at the end of the chamber. These red fumes

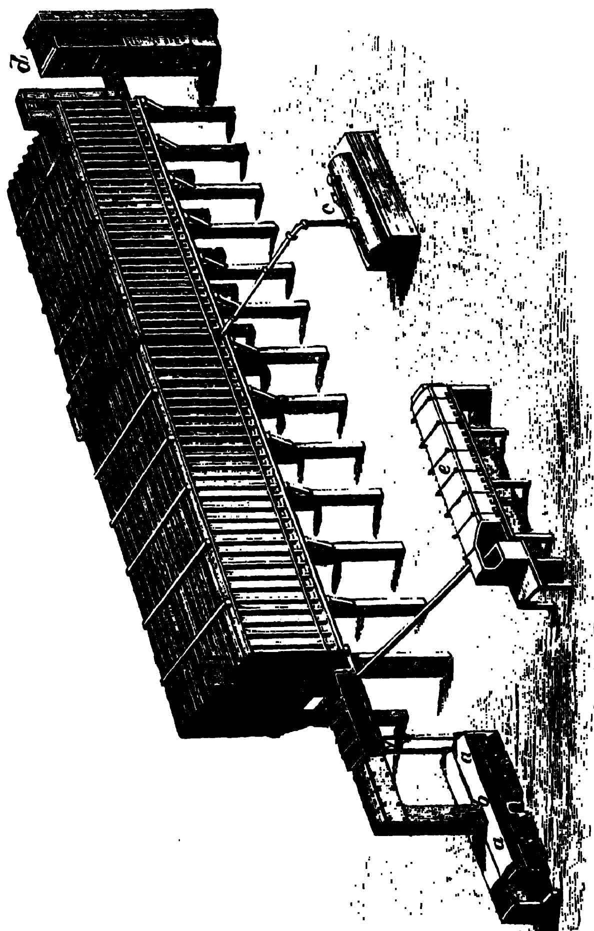


Fig. 100.

are absorbed by an arrangement called a Gay-Lussac tower, down which cold and concentrated sulphuric acid is allowed to trickle slowly before the waste gases pass into the upcast shaft.

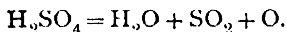
The red fumes are used again in the initial stages of the process by allowing the *nitrated sulphuric acid* obtained from the Gay-Lussac tower to trickle down another tower called the Glover tower, or denitrating tower, together with the weak chamber acid. The hot gases from the pyrites kilns are first allowed to pass into the Glover tower, and the sulphur dioxide not only robs the nitrated acid of its nitrous fumes, but the hot gases are themselves cooled before they enter the leaden chamber, and the weak acid is at the same time made stronger by being deprived of a portion of its water which passes into the chamber as steam, and assists in the subsequent formation of sulphuric acid.

The acid, as made in the leaden chambers, called "chamber acid," is a dilute acid of sp. gr. 1.6. To obtain a stronger acid, this is first evaporated in leaden pans until the sp. gr. reaches 1.72, when the acid is known in commerce as Brown Oil of Vitriol or B.O.V. It cannot be further concentrated in leaden pans, because the stronger acid attacks the lead. The B.O.V. must, therefore, be further concentrated in platinum or glass vessels. The acid thus obtained is far from pure; not only does it contain small amounts of nitrous fumes and sulphur dioxide, but also arsenic derived from the iron pyrites, which are burnt as a source of sulphur, and lead sulphate derived partly from the leaden chamber, but more particularly from the leaden concentrating pans. To obtain the pure acid the commercial B.O.V. must be distilled. The volatile impurities pass over in the first third of the distillate, after which the pure concentrated acid may be collected in a fresh receiver. This acid is free from nitrous fumes, arsenic, and lead, and also from the organic matter which renders the impure acid brown.

Properties.—The acid thus purified by distillation still contains about 2 per cent of water which cannot be removed by this process. If, however, the distillate be cooled, the pure acid, H_2SO_4, separates out in the form of crystals, which melt at 10.5°. The strong acid is an oily liquid having a specific gravity of 1.854 at 0°.

Effects of Heat.—When the pure acid is heated it begins to fume at 30°, owing to a partial decomposition into H_2O and SO_3. This decomposition increases until the boiling point 338° is reached, when a liquid remains which contains 98.4 to 98.8 per cent of the pure acid, which distils without change.

When very strongly heated, as, for example, when the acid is allowed to fall, drop by drop, into a red-hot platinum flask, filled with pumice stone, it decomposes into sulphur dioxide, oxygen, and water.



$$H_2SO_4 = H_2O + SO_2 + O.$$

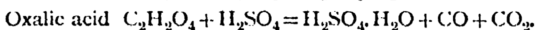
The first two may be absorbed by water and the oxygen gas collected.

Affinity for Water.—When sulphuric acid is mixed with water, great heat is evolved owing to their chemical combination, and a contraction in volume takes place. So much heat is thus given off that it is dangerous to add water quickly to a large bulk of the acid, the two combining with explosive violence. In diluting the acid, therefore, the strong acid should be gradually poured into the requisite volume of water contained in a thin glass flask, the mixture being shaken or stirred during the addition of the acid. Owing to its great affinity for water, strong sulphuric acid is used for drying gases. For this purpose the gas is best passed through a tube containing pumice stone which has been boiled in the strong acid. This method cannot, of course, be used for drying such gases as ammonia, which combine with the acid. Small pieces of well burnt quick-lime must then be substituted. Strong sulphuric acid is also used for keeping a dry atmosphere in the closed space of desiccators, either at the ordinary pressure or *in vacuo.* Solid substances are enclosed in this dry space to be kept dry, or to be deprived of the last traces of moisture.

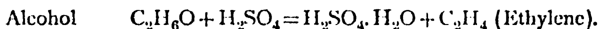
Not only does strong sulphuric acid combine energetically with water itself, but it also abstracts the elements of water from many organic compounds, thus :—



Formic Acid $CH_2O_2 + H_2SO_4 = H_2SO_4.H_2O + CO.$



Oxalic acid $C_2H_2O_4 + H_2SO_4 = H_2SO_4.H_2O + CO + CO_2.$



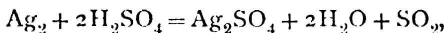
Alcohol $C_2H_6O + H_2SO_4 = H_2SO_4.H_2O + C_2H_4$ (Ethylene).

We shall see (Expt. 120) that the acid abstracts the elements of water from such carbohydrates as sugar in a similar manner.

Crystalline Hydrate of Sulphuric Acid.—Sulphuric acid forms a definite crystalline compound with water, having the composition $H_2SO_4.H_2O$. A mixture of the acid with

water in equal molecular proportions solidifies to a mass of prismatic crystals at 7.5°.

Action on Metals.—The concentrated acid does not act on many metals in the cold although it does so when heated. Copper, mercury, antimony, bismuth, tin, lead, and silver are attacked by the hot acid with evolution of sulphur dioxide, thus :—



$$Ag_2 + 2H_2SO_4 = Ag_2SO_4 + 2H_2O + SO_2,$$

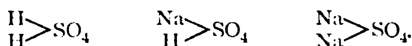


$$Cu + 2H_2SO_4 = CuSO_4 + 2H_2O + SO_2.$$

Gold and platinum are unacted upon even by the boiling acid, and this acid is therefore used for *parting* or separating silver and gold. Such metals as zinc, iron, manganese, and magnesium are dissolved by the dilute acid in the cold with evolution of hydrogen and the formation of sulphates.

The Sulphates

Sulphuric acid, like sulphurous acid, is a dibasic acid, and therefore forms two series of salts, viz. the acid salts and normal salts, thus :—

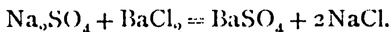


$$\begin{matrix}H\\H\end{matrix}>SO_4 \qquad \begin{matrix}Na\\H\end{matrix}>SO_4 \qquad \begin{matrix}Na\\Na\end{matrix}>SO_4.$$

Many sulphates are found in nature, *e.g.* Gypsum, $CaSO_4 . 2H_2O$, Heavy spar, $BaSO_4$, Celestine, $SrSO_4$, Glauber salts, $Na_2SO_4 . 10H_2O$, Epsom salts, $MgSO_4 . 7H_2O$. Crystallised copper sulphate, $CuSO_4 . 5H_2O$, is known as blue vitriol. $ZnSO_4 . 7H_2O$, and $FeSO_4 . 7H_2O$, represent the corresponding crystallised sulphates of zinc and iron known as white and green vitriol respectively, from the colour of the crystals.

Barium and lead sulphates are insoluble in water. Calcium and strontium sulphates are slightly soluble, whilst most other sulphates are soluble.

Tests for Sulphates.—(1) All soluble sulphates, on the addition of barium chloride, give a white precipitate of barium sulphate insoluble in dilute hydrochloric acid.

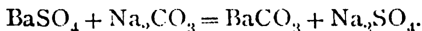


$$Na_2SO_4 + BaCl_2 = BaSO_4 + 2NaCl.$$

(2) If a sulphate is mixed with sodium carbonate and heated on charcoal in the reducing blowpipe flame a sulphide is produced. If the fused mass is laid on a clean silver coin and

moistened with water, a black stain of silver sulphide is formed on the coin.

(3) Insoluble sulphates, such as barium sulphate, may be decomposed by boiling with sodium carbonate, when soluble sodium sulphate is produced, which may be filtered and tested for with barium chloride after acidifying with hydrochloric acid.



$$BaSO_4 + Na_2CO_3 = BaCO_3 + Na_2SO_4.$$

What we have learnt

In our twentieth Lesson we have learnt that sulphur dioxide may be prepared (1) by the action of hot concentrated sulphuric acid on copper; (2) by burning sulphur or iron pyrites in the air; (3) by heating sulphur or charcoal with strong sulphuric acid; (4) by the action of acids on sulphites.

We have seen that sulphur dioxide is a colourless, pungent-smelling gas, about twice as heavy as air, and very soluble in water, with which it combines to form sulphurous acid. We have seen how it may be liquefied, and how its composition may be determined.

Sulphurous acid is a dibasic acid, and therefore forms two series of salts, viz. normal sulphites, M'_2SO_3; acid sulphites, $M'HSO_3$, where M′ stands for any monad metal.

Sulphur trioxide is prepared by passing sulphur dioxide and oxygen over heated platinised asbestos. It is a white solid compound, which rapidly absorbs water with formation of sulphuric acid. This latter compound is manufactured on the large scale by passing (1) sulphur dioxide, (2) steam, (3) air, and (4) a small amount of nitric acid vapour into a capacious leaden chamber, where the nitrous fumes act as a carrier of the atmospheric oxygen to the sulphur dioxide, which is thus oxidised to sulphuric acid in the presence of steam. Sulphuric acid is a heavy oily liquid possessing very great affinity for water, the component elements of which it will abstract from many compounds. Like sulphurous acid, sulphuric acid is dibasic, and forms two series of salts, M'_2SO_4, $M'HSO_4$. Many of the normal salts are found in nature. All soluble sulphates give a white precipitate with a solution of barium chloride, insoluble in hydrochloric acid.

Exercises on Lesson XX

1. How is sulphur dioxide prepared (1) in the laboratory, (2) on the manufacturing scale? State its principal properties, and the method of determining its composition.

2. What is the action of strong sulphuric acid on carbon, on sulphur, on oxalic acid, on alcohol, and on formic acid?

3. How may sulphur dioxide be liquefied?

4. What weight of sulphur is contained in 2000 litres of sulphur dioxide, measured at 17° R. and 785 mm.?

5. Give the formulæ of the sodium, calcium, and ammonium salts of sulphurous acid.

6. How is sulphur trioxide prepared? What special precautions must be taken in making it?

7. Describe the manufacture of sulphuric acid.

8. How would you obtain sulphuric acid free from lead, arsenic, and nitrous fumes from a sample of B.O.V.?

9. What are leaden chamber crystals, and what is the action of steam on them? Give formulæ and equations.

10. Explain the action of the nitric acid vapour which is used in the manufacture of sulphuric acid.

11. What weight of sulphuric acid may be obtained by burning two tons of sulphur, supposing it to be completely oxidised to sulphuric acid?

12. Give the tests by which you would recognise sulphur, sulphuretted hydrogen, a sulphite, and a sulphate respectively.

LESSON XXI

CARBON AND ITS ALLOTROPIC MODIFICATIONS—CARBON MONOXIDE—CARBON DIOXIDE—METHANE—ACETYLENE—ETHYLENE—COAL-GAS AND FLAME.

Carbon

Occurrence.—Carbon is an essential constituent of every animal and vegetable body, from the most minute and simple organism up to the largest and most complicated.

The number of the known compounds of carbon with three elements, viz. hydrogen, oxygen, and nitrogen, is far larger than that of all the other elements put together; moreover, many of them possess so complicated a composition and are so different in their properties from the compounds of other elements, that they are usually considered as forming a separate branch of the science, and this branch is called *organic chemistry*. Still the study of carbon and some of its simpler compounds cannot be omitted from even an introduction to *Inorganic Chemistry*, such as the present work, because carbon itself possesses most interesting properties, and its simpler combinations, which may be considered to be inorganic compounds, play so important a part in nature.

Whilst carbon itself occurs only in small amount, its compounds are found to exist in large quantity. It exists combined with oxygen in the atmosphere as carbonic acid gas, or carbon dioxide, CO_2, and although its relative proportion is small (only about 4 in 10,000 vols. of air), the absolute amount is enormous, reaching several billions of tons. Besides, combined

with lime, CaO, as limestone, $CaCO_3$, and as magnesian limestone or dolomite, $(CaMg)CO_3$, it forms whole mountain ranges; whilst as chalk and marble it exists in very large quantities. Chalk and coral have been formed, partly during past geological ages, through the agency of minute organisms living in sea-water. In addition to these, other enormous masses of carbon compounds exist in the living forms, animal and vegetable, existing on the earth's surface. Combined with hydrogen, carbon exists in rock oil or petroleum, benzene and coal gas, whilst in further combination with oxygen it occurs in vegetable oils, fats, sugar, starch, and woody fibre.

EXPT. 120.—A striking experiment shows that white crystalline sugar contains large quantities of carbon. Let us place an ounce of lump-sugar in a large cylinder, and pour upon it enough hot water to cover it, and then add about double the volume of strong sulphuric acid, stirring up the mixture with a glass rod. In a few seconds the colourless liquid will become brown, then black, and in a few minutes it will boil up, the jar becoming filled with a coal-black mass of carbon. Sugar is a carbohydrate, and the strong sulphuric acid has abstracted from it the elements of water, leaving only carbon.

Allotropic modifications of Carbon

Carbon, like sulphur, is remarkable as existing in three totally different solid forms: (1) diamond, (2) graphite, (3) charcoal; hence carbon is said to exist in three allotropic modifications. No one has yet succeeded in converting graphite or charcoal into diamond. How, then, do we know that the colourless sparkling gem, the hardest of all known substances, is the same chemical substance as soft black graphite, commonly called blacklead, and used for making pencils and polishing our stoves, and that this latter substance is again the same as soft porous charcoal got by heating wood, or as soot or lampblack, which is nearly the same thing as charcoal? No one could have believed that these three substances consist of carbon until experiment proved this to be the case. Let us see how this was done.

The Diamond, the purest form of Carbon, Crystallised Carbon

The **diamond** has for ages been valued as a precious stone on account of its brilliant lustre and its great hardness (adamant); but its composition remained unknown until about a hundred years ago. Experiments had indeed been previously made, which showed that diamonds could be burned; thus diamonds placed in the focus of a powerful burning-glass were found to disappear, but what became of them was not known. Then diamonds and rubies (another kind of precious stone) were heated together in a furnace, and the diamonds disappeared, whilst the rubies remained unaltered—this also could not be explained. Afterwards it was noticed that if the diamonds were heated in a perfectly closed vessel they did not disappear. No one was able to explain these facts until Lavoisier made the following experiment about the end of last century. He placed a diamond in a glass vessel containing pure air over mercury, and then heated the diamond by means of a burning-glass; the diamond took fire and burnt completely away, leaving only a mere trace of ash, and on examining the air after the combustion he found that it turned lime-water milky, and, therefore, contained carbonic acid gas, which, as we have seen, is always formed when carbon itself, or a carbon compound, is burnt in the air or in oxygen. But it may properly be said, it is true, that this experiment shows that diamond contains carbon, but it does not prove that it consists of carbon and nothing else. This, however, was ascertained by Davy in 1814, because he observed that no trace of water is formed when a diamond is burnt in pure oxygen, so that this gem can contain no hydrogen. Then further experiments proved that if we take the same weights, say 12 parts, of diamond, of graphite, of charcoal, they all yield exactly the same weight (44 parts) of carbonic acid gas. So now we know that each of these three substances consists of nothing else but carbon.

Carbon in the free state exists only in small quantities in nature. The diamond is a rare and valuable substance; it crystallises in forms derived from the regular octohedron (see

Fig. 101), and is found in a peculiar rock or in alluvial deposits in Brazil, South Africa, the Urals, and elsewhere. Its specific gravity is about 3.5. We do not know how diamonds have been formed, nor how to make them artificially.



Fig. 101.

Graphite. — Graphite, the only other form of naturally occurring free carbon, is a soft black substance, of specific gravity about 2.2, and is found in many localities, the most famous of which is Borrowdale in Cumberland, but the mines there are exhausted. It has also been found in Siberia, in many places in North America, especially in California. It occurs in granite, gneiss, and other crystalline rocks; its mode of formation is likewise unknown. It sometimes occurs in crystals, but not in the same form as diamond.

Charcoal is the amorphous or non-crystalline form of carbon. It is obtained by the decomposition of organic bodies. Thus, when wood is heated strongly in absence of air, charcoal is left behind as a black porous mass, the volatile portions of the wood escaping. There are several varieties of charcoal—they are (1) lampblack; (2) gas carbon; (3) coke; and (4) animal charcoal; (5) wood charcoal.

Wood charcoal is made by arranging pieces of wood in a heap, covering the heap with soil, leaving an air hole in the centre, and then kindling the wood at the bottom; care must be taken only to allow a small amount of air to enter, otherwise the whole heap would be completely burnt and only white ashes left. Charcoal is very porous, and, though heavier than water (sp. gr. about 1.8), it floats on this liquid, because its pores are filled with air; but if we extract this air by means of an air-pump, the pieces of charcoal will be seen to sink in water. This porous nature of charcoal is a valuable property, as it enables charcoal to absorb large quantities of gases and colouring matters.

EXPT. 121.—Thus if a few bits of charcoal, which have been previously heated in a flame, be passed up into a tube filled with dry ammonia gas collected over mercury, it is soon

seen by the rise of the mercury in the tube that the gas is absorbed. Charcoal can absorb 90 times its bulk of NH_3. Other gases are also absorbed by charcoal, but in smaller quantity. Thus it absorbs 9 times its volume of oxygen, and this is the reason why charcoal acts as a powerful disinfectant. If a piece of animal flesh be buried in charcoal powder, no unpleasant smell is noticed, the putrefactive gases which are given off from decomposing animal matter are absorbed and oxidised to carbonic acid and water by the oxygen taken up by the porous charcoal.

Animal charcoal or bone black is made by charring bones in iron cylinders; it contains, together with charcoal, the inorganic constituents of the bone (phosphate of lime). This is largely used for decolouring raw sugar; the brown syrup is allowed to run over bone black contained in iron cylinders, it passes out at the bottom of the column perfectly colourless.

EXPT. 122.—The decolourising power of animal charcoal is well shown by adding a little blue solution of indigo to some boiling water, and then shaking this up with some bone black. After a short time the liquid is passed through a filter, when it is seen to be colourless; some of the blue liquid, without addition of bone black, poured on to another filter is as darkly coloured after filtration as before.

Lampblack is a pure form of soot, made by imperfectly burning turpentine, resin, tallow, oil, or pitch. It is used for making black paint and printers' ink. Lampblack is not pure carbon, as it contains oily matter. To obtain pure carbon from it, the black must be not only strongly heated, but ignited in a current of chlorine gas; this is the only way of getting rid of all the hydrogen, as it combines with the chlorine to form hydrochloric acid, leaving pure carbon behind, for lampblack, carefully made, contains no inorganic or mineral matter.

Coal is the result of the decay and gradual decomposition of vegetable matter once growing on the earth's surface. This has been going on for ages. Coal is not pure carbon; it contains not only the mineral matter which the vegetation contained, but much more which has been added since the vegetation grew. Besides, it contains more or less hydrogen, as may be seen from the blaze which ordinary coal gives in the

fire. This part is made use of in the manufacture of coal gas for illuminating purposes; no gas can be made by heating charcoal or coke in a retort. There are many varieties of coal. Cannel (or candle) coal is richest in hydrocarbons; anthracite coal poorest. Coal also contains sulphur (about 2 per cent on the average), generally as iron pyrites or "coal brasses," FeS_2. When coal burns, this sulphur also burns, forming sulphur dioxide, and this oxidises in contact with the atmospheric oxygen, and combines with moisture, forming sulphuric acid. This is very deleterious and harmful to vegetable life, and it likewise attacks and destroys stone buildings. Many hundreds of tons of this acid are thrown into the atmosphere in London, where millions of tons of coal are burnt every year.

Carbon is called a reducing agent.—What do we mean by that? An experiment will show us.

EXPT. 123.—Take a little black oxide of copper, and mix with it some powdered charcoal; heat the mixture in a test tube fitted with a delivery tube, which dips under some clear lime-water. What is observed? Gas is given off, and this, passing through the lime-water, makes it milky. So carbonic acid gas is given off. What change has here occurred? If we examine the residue it will be seen to contain bright red particles of copper. The carbon has *reduced* the oxide—thus $2CuO + C = 2Cu + CO_2$. Both coal and coke are largely used in metallurgical operations for this reason. Iron ore is smelted with coal and cast iron is produced. Many other metals are manufactured from their ores by using carbon as a reducing agent.

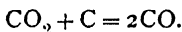
THE OXIDES OF CARBON, CO AND CO_2

Carbon Monoxide, or Carbonic Oxide Gas

FORMULA CO. MOLECULAR WEIGHT 27.8. DENSITY 13.9

This gas is formed when carbon is burnt in a limited supply of oxygen. The blue lambent flame so often seen at the top of a red-hot coal fire is that of carbon monoxide formed by the

action of the red-hot fuel on carbon dioxide produced by the combustion of the fuel at the lower part of the fire; thus—



$$CO_2 + C = 2CO.$$

The carbon monoxide burns again to CO_2 when it reaches the top of the fire, and there comes into contact with the oxygen of the air. This reaction serves as a means of preparing this compound. For this purpose a piece of iron gas-piping filled with charcoal and furnished with corks and tubes as shown in Fig. 102 is placed in a tube furnace and connected with a bottle containing marble and water from which carbon dioxide can be evolved by the addition of hydrochloric acid. As soon as

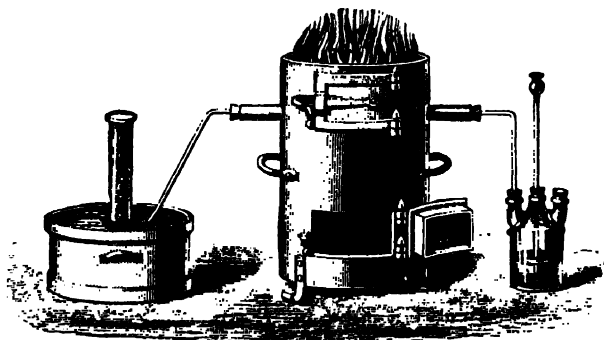


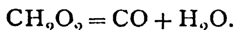
Fig. 102.

the piping is red-hot a slow current of CO_2 is allowed to pass over the heated charcoal, when carbon monoxide is evolved and can be collected over water as shown in the figure.

EXPT. 124.—Carbon monoxide can be more conveniently prepared from several compounds of carbon. Thus if crystallised oxalic acid ($C_2H_2O_4$) be heated in a flask with strong sulphuric acid, a mixture of equal volumes of CO and CO_2 are evolved (see equation, p. 212), and if these two gases be collected over water they can be readily separated by shaking the mixture with caustic soda, when half the volume will disappear owing to the combination of CO_2 with the soda, whilst the CO remains unabsorbed. The explanation of this mode of preparation is that hot sulphuric acid removes the elements of water (H_2O)

from oxalic acid, leaving the residue C_2O_3, which cannot exist alone and at once splits up into CO and CO_2.

EXPT. 125.—A method by which carbon monoxide is obtained unmixed with carbon dioxide, is to heat formic acid (CH_2O_2) or sodium formate ($CHNaO_2$) with strong sulphuric acid, when water (H_2O) is taken up by the acid and CO is evolved as a gas—



$$CH_2O_2 = CO + H_2O.$$

Properties.—Carbon monoxide is a colourless, tasteless gas. It acts as a strong poison when inhaled even in small quantities, and the fatal effect often noticed of breathing the air of rooms in which charcoal is burnt in a chauffer, or of gases from limekilns or brickkilns, is due to the presence of this gas. Like all other gases, this compound can be liquefied, but to effect this a much lower temperature is required than in the case of carbon dioxide, as liquid carbon monoxide boils at $-193°$, and the gas must, therefore, be cooled below this point before it liquefies. The gas is rather lighter than air and cannot be collected either by upward displacement like hydrogen, or by downward displacement like carbon dioxide, but it can be collected over water as it is only very slightly soluble in that liquid.

Carbon monoxide burns, when a light is brought to it, with a characteristic blue lambent flame with formation of carbon dioxide, $CO + O = CO_2$. This serves as a test for this gas.

EXPT. 126.—Pour some clear lime-water into a bottle filled with the gas and observe that, when shaken, the lime-water remains clear, then bring a light to the mouth of the bottle, observe the flame, and when it has burnt out, shake up the lime-water and notice that it becomes milky, and this milkiness disappears on the addition of a few drops of hydrochloric acid.

Carbon monoxide can be separated from other gases by bringing it into contact with cuprous chloride, CuCl, when it is absorbed.

Determination of Composition

The composition of the gas is ascertained by exploding it mixed with oxygen (by an electric spark); in this case moisture must be present, as combination does not occur when the gases

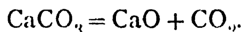
are perfectly dry. One hundred vols. of carbon monoxide yield 100 vols. of carbon dioxide and require 50 vols. of oxygen. But, as carbon dioxide contains its own volume of oxygen, carbon monoxide must contain half its volume of oxygen, or 2 vols. weighing 27.8, contain 1 vol. of oxygen weighing 15.9; its formula is, therefore, CO.

Carbon Dioxide

FORMULA CO_2. MOLECULAR WEIGHT 43.7. DENSITY 21.85

Occurrence.—This gas, as we have seen, is formed whenever carbon or any of its compounds burn in excess of air or oxygen. It not only exists in the free state in the air, but is evolved from the earth, especially near volcanoes, and it accompanies the water in many mineral springs. Moreover, it occurs, as has been said, in combination with lime and magnesia, as magnesian limestone or dolomite, and with lime as limestone, coral, chalk, marble, and calcspar. It is not only given off by animals in breathing (the expired air from the human lungs contains about 4 per cent of this gas), but is evolved in the process of decay of animal as well as of vegetable matter, and in the fermentation of sugar. Hence, carbon dioxide often accumulates at the bottom of caverns and of old wells and mines, as well as in brewers' vats, and also in coal pits, where it is known as *choke-damp* or *after-damp* (damp is the German *dampf*, vapour), formed by the combustion of *fire-damp* (see p. 230).

Preparation.—If we want large volumes of carbon dioxide we may use the gases coming off from burning coke, or from limekilns; in these, chalk or limestone, calcium carbonate ($CaCO_3$), is heated in a draught of air, solid quicklime, CaO, remains behind, and CO_2 comes off as a gas.



$$CaCO_3 = CaO + CO_2.$$

But neither of these methods is good for laboratory purposes, and on the small scale we always prepare this compound by acting on chalk or marble with an acid—almost any acid may be used for this purpose, but hydrochloric acid is the best.

EXPT. 127.—Place some lumps of marble in a flask, add

some water, and then pour on to this some hydrochloric acid (HCl) through the tube funnel. Effervescence soon begins, owing to the rapid disengagement of the gas, which may be collected either over water, or, as it is half again as heavy as air, by *downward displacement*, as shown in Fig. 103.



$$CaCO_3 + 2HCl = CaCl_2 + H_2O + CO_2.$$

The same kind of change occurs if other acids, such as acetic acid (vinegar), sulphuric, or nitric acids are added, but then the calcium salt corresponding to the acid is formed. Sulphuric acid is, however, unsuitable for the preparation of CO_2 from marble, because the calcium sulphate which is produced is only slightly soluble in water, and it forms a coating on the marble, thus preventing the acid coming in contact with it, and thus stopping the evolution of gas. Similarly, any other carbonate, such as carbonate of soda (washing soda), or carbonate of potash (pearl-ash), may be used instead of marble, but this latter substance answers best, and is cheapest.

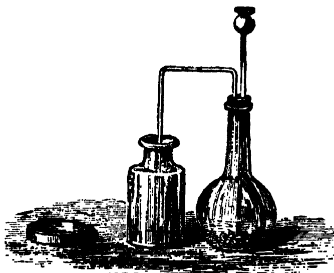


Fig. 103.

Properties.—Carbon dioxide is colourless, and has a slightly acid taste. It is a heavy gas, being 22 times as dense as hydrogen. We can, therefore, syphon it like water, or pour it from one vessel to another (see Expt. 2); it does not support ordinary combustion, and the flame of a taper as well as that of burning phosphorus are extinguished when plunged into the gas. If, however, we heat a bit of potassium in a flask filled with the dry carbonic acid gas, the metal is seen to take fire and burn. What happens here is that the carbon dioxide is decomposed into oxygen, which unites with the potassium to form white fumes of oxide of potassium and black carbon, which deposits on the side of the glass flask.

Solubility of Carbon Dioxide.—Under the ordinary

atmospheric pressure carbon dioxide is soluble in water; the maximum which can be dissolved by 1 gram of water at 0° is 1.8 vols., whilst at 20° only 0.9 vols. (or half the former amount) dissolves. If, however, the pressure be increased—that is, if the gas be pumped into water under pressure, more of the gas is taken up by the water, and when the pressure is removed the gas is evolved. This is well seen in the case of ordinary soda water, which contains the gas in solution pumped in under a pressure of about 4 atmospheres.

EXPT. 128.—If we insert through the cork of a bottle of soda water a small screw tap, and attach to the end a piece of caoutchouc tubing, we can, by opening the cork, easily collect the carbonic acid gas which has been in solution in the water, but escapes when the extra pressure is removed. It is easy to calculate how much gas will be dissolved in water under increased pressure, when we remember that experiment has shown that if we double the pressure we double the *weight* of gas dissolved; and because the volume occupied by any gas under varying pressure is inversely proportional to that pressure, the *volume* of gas absorbed will remain constant whatever be the pressure. Thus if, at the ordinary atmospheric temperature and pressure, 1 gram of water dissolves 2 milligrams of CO_2, it will dissolve 4 mgm. (or double the amount) when the pressure reaches 2 atmospheres, or is also doubled. If soda water is made under a pressure of 5 atmospheres, and a bottle holds 200 c.c. of water, under the pressure of 760 mm. the volume of CO_2 which this quantity of water can dissolve amounts to 250 c.c.; we see that we can collect 1000 c.c. of gas, and this is the difference between the saturating quantity under the pressure of 5 atmospheres, and that under that of 1 atmosphere.

As CO_2 is formed during the process of fermentation—or the conversion of sugar into alcohol by means of a ferment such as yeast—we find that liquors, such as beer and champagne, in which the process of conversion of sugar into alcohol is not complete before they are bottled, become saturated with carbon dioxide under an increased pressure, and when the pressure is diminished by withdrawing the cork, the liquid effervesces from escape of the gas.

Liquid Carbonic Acid Gas.—Like all gases, carbon dioxide can be condensed to a liquid by the application of cold and pressure. The boiling point of the liquid under ordinary atmospheric pressure is $-78°$; cooled still further it solidifies to a colourless ice-like mass. If brought under a pressure of 35.5 atmospheres at $0°$, the gas also liquefies, and if the liquid be allowed to escape into the air through a fine nozzle attached to the steel cylinder into which it has been pumped, part of the liquid at once evaporates, and so much heat is thereby absorbed that the rest solidifies. A brass box is, for this purpose, attached to the nozzle of the steel cylinder, and this, after the liquid has been allowed to enter, is seen to be filled with a white snow-like substance which is solid carbonic acid. Liquid carbon dioxide is now a commercial substance, sold at 1s. per lb., being employed for a variety of purposes. The solid is used for the production of very low temperatures; for this purpose the snow-like powder is mixed with ether, and the mixture placed in a vacuum; by this means a temperature as low as $-100°$ is attained, and mercury can thus be easily frozen.

Composition of Carbon Dioxide.—How is the composition of carbon dioxide ascertained? In the first place, if we burn a piece of charcoal in a measured volume of oxygen, and take care that neither any oxygen nor any carbon dioxide formed in the combustion escapes, we shall find that no change in the volume of the gas before and after the experiment has occurred. This shows that carbon dioxide contains its own volume of oxygen, for if it did not do so a change of volume must have taken place. Now we know that one volume of carbon dioxide weighs 22, when the same volume of hydrogen weighs 1, or 2 volumes of carbon dioxide weigh 44; but this contains its own bulk (2 volumes) of oxygen, and the 2 volumes of oxygen weigh $2 \times 16 = 32$, so that the weight of carbon contained in 2 volumes of carbon dioxide must be the difference (because it contains nothing else), or $44 - 32 = 12$; this latter number is, however, the atomic weight of carbon, hence carbon dioxide is composed of 12 parts by weight of carbon, and 32 parts by weight of oxygen, or its formula is CO_2.

Another method of ascertaining the composition of carbon dioxide is to burn a known weight of pure carbon, such as

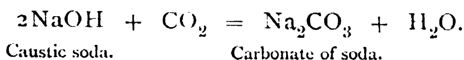
diamond or graphite in a current of oxygen gas, collecting and weighing the carbon dioxide formed. This determination has been made by several chemists with great care.

In the first place, the accurately weighed quantity of diamond or graphite contained in a small boat of platinum is placed inside a porcelain tube, which can be strongly heated in the furnace. The oxygen is contained in a gas-holder, which is connected with the porcelain tube by a series of drying tubes by which the gas is rendered perfectly dry and pure before it reaches the diamond. At the other end are placed tubes and bulbs containing caustic potash to absorb the carbon dioxide formed by the combustion of the diamond, whilst other tubes contain pumice stone moistened with sulphuric acid to retain any moisture which the gas might carry away. Of course these tubes are carefully weighed, and then the apparatus put together, great care being taken that all the joints are perfectly air-tight. After the whole has been filled with dry oxygen, the porcelain tube is brought to a red heat, the combustion begins, and the experiment is allowed to proceed. All the carbon dioxide thus generated is absorbed by the caustic potash, and, as the oxygen gas is dried both on entering and on leaving the apparatus, the gain in weight of the tubes gives the exact weight of carbon dioxide produced by the combustion of the diamond. As, however, even this purest form of carbon contains a certain amount of mineral matter which is left behind in the platinum boat as ash, it is necessary, in order to obtain the exact amount of carbon burnt, to weigh the boat after the experiment and to deduct the weight of the ash from that of the diamond taken. Another necessary precaution is to place some copper oxide in the half of the porcelain tube nearest the bulbs and tubes, in order that any carbon monoxide (CO) which might be formed and would escape absorption by the potash, shall be oxidised to CO_2. Many very careful experiments made in this way showed that 11.9 parts by weight of carbon combine with 31.8 parts of oxygen to form this gas; that is, the relation between the number of atoms of carbon and oxygen is 1 to 2, or the formula of carbon dioxide is, as its name implies, CO_2.

EXPT. 129. **Carbonic Acid and the Carbonates.**—If a blue litmus paper be plunged into water in which carbon

dioxide is dissolved, the blue colour is changed to red, showing the presence, of an acid, whilst dry CO_2 does not effect this alteration. This shows that the aqueous solution contains an acid. Carbonic acid, $H_2O + CO_2 = H_2CO_3$, is a dibasic acid (see p. 205), but it is very unstable and cannot be obtained in the pure state. On the other hand, it forms a series of stable salts termed the carbonates.

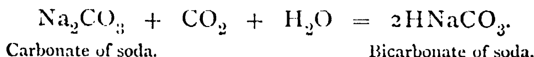
EXPT. 130.—When carbon dioxide is passed into a solution of caustic soda it is rapidly absorbed, and carbonate of soda is formed.



$$2NaOH + CO_2 = Na_2CO_3 + H_2O.$$

Caustic soda. Carbonate of soda.

If an excess of carbon dioxide be used, or if carbon dioxide is passed into a solution of the preceding salt, a neutral solution is obtained and another salt, viz. bicarbonate of soda, is formed.



$$Na_2CO_3 + CO_2 + H_2O = 2HNaCO_3.$$

Carbonate of soda. Bicarbonate of soda.

We thus see that two classes of carbonates exist—one, called the normal salt, in which both atoms of hydrogen in carbonic acid, H_2CO_3, are replaced by metal, and the other called bicarbonate or the acid salt, in which only one atom is thus replaced.

EXPT. 131.—Let us next pass carbon dioxide through clear lime-water; at first a white precipitate of insoluble calcium carbonate ($CaCO_3$, see Expt. 4), soluble in hydrochloric acid, is thrown down, and this serves as a test for carbon dioxide. After the gas has passed through for a longer time, this white precipitate re-dissolves and the liquid becomes clear again owing to the formation of a soluble bicarbonate. This compound is destroyed when the liquid is boiled, CO_2 is given off and white carbonate of lime ($CaCO_3$) is precipitated (see Expts. 58 and 59). The carbonates of the alkali metals, potassium and sodium, and of ammonium are soluble in water; the normal carbonates of the other metals are insoluble in water. This latter fact is seen by adding a solution of carbonate of soda to

a soluble salt of any metal, such as sulphate of zinc, sulphate of copper, or acetate of lead.

Compounds of Carbon with Hydrogen

These compounds termed the hydrocarbons are extremely numerous. They exist as solids, such as paraffin wax; liquids, such as turpentine; and as gases. Of this latter class only three, and those most simple, will here be mentioned, viz. (1) methane or marsh gas, CH_4, (2) Acetylene C_2H_2, and (3) ethylene or olefiant gas, C_2H_4.

Methane or Marsh Gas

FORMULA CH_4. MOLECULAR WEIGHT 15.9. DENSITY 7.95

This gas is interesting as occurring in coal-pits and causing, when mixed with air and the mixture fired, the serious explosions which too often occur in coal mines. The pitmen term this gas "fire-damp," and the carbonic acid gas which results from the explosion "after-damp." Methane is formed by the gradual decomposition of organic matter such as leaves, and the gas may be seen to arise in bubbles from stagnant pools and marshes, and from this the name marsh gas is derived. This compound is also a constituent of coal gas, and is not only found as fire-damp in coal-pits, but is evolved in such large quantities from the oil springs, especially in America, that it is carried from the springs for some miles to cities where it is used as a source of heat.

EXPT. 132. **Preparation.**—If we want to prepare this gas in the laboratory we make use of the following reaction—

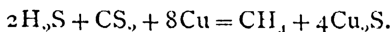


$$NaC_2H_3O_2 + NaOH = Na_2CO_3 + CH_4.$$

Sodium acetate and caustic soda give sodium carbonate and marsh gas. For this purpose it is best to heat a mixture of 1 part of acetate of soda with 4 parts of soda lime (a mixture of caustic soda and lime). The heat required is greater than an ordinary glass flask will stand, so it is necessary to use a

tube of hard glass, closed at one end and fitted with a cork and delivery tube at the other.

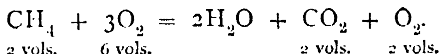
Marsh gas cannot be obtained by the direct union of carbon and hydrogen, but is formed when a mixture of sulphuretted hydrogen (SH_2) and the vapour of carbon disulphide (CS_2) are passed together over red-hot copper.



$$2H_2S + CS_2 + 8Cu = CH_4 + 4Cu_2S.$$

Properties.—Marsh gas is colourless and tasteless and can be condensed to a liquid only by very great pressure; the liquid boils at $-164°$. It has only about half the density of air and used to be called light carburetted hydrogen; it is very inflammable, burning with a faint blue flame, forming carbon dioxide and water. When mixed with twice its volume of oxygen or with ten times its volume of air the mixture ignites on application of a flame and a violent explosion occurs; hence the danger of sudden outbreaks of this gas from the coal measures, and the necessity of using, in such "fiery mines," as they are termed, a safety-lamp (see p. 238) which cannot cause the ignition of the combustible gaseous mixture.

Composition.—Why do we give the formula CH_4 to this compound? The answer is given by the following: Let us take 2 volumes of this gas and mix it with 6 volumes of oxygen in a eudiometer (see p. 92); we then find that after passing an electric spark through the mixture the 8 volumes have been reduced to 4 volumes. Next let us



$$\underset{2\ \text{vols.}}{CH_4} + \underset{6\ \text{vols.}}{3O_2} = 2H_2O + \underset{2\ \text{vols.}}{CO_2} + \underset{2\ \text{vols.}}{O_2}.$$

absorb the carbon dioxide formed by the above combustion by means of caustic soda; we find that 2 volumes of oxygen gas remain. Hence 4 volumes of oxygen were needed to burn the carbon and hydrogen contained in 2 volumes of methane, of which 2 have gone to burn the carbon to carbon dioxide and 2 to burn the hydrogen to water. Therefore 2 volumes of methane must contain 4 volumes of hydrogen weighing 4, and the weight of carbon (viz. 11.9 parts) which is contained in two volumes of CO_2, and since its density is 7.95, we conclude that CH_4 is its molecular formula.

Acetylene

FORMULA C_2H_2. MOLECULAR WEIGHT 25.8. DENSITY 12.9

This gas is of interest because it is formed by the direct union of its elements, whilst the other two compounds are produced indirectly. Carbon and hydrogen can only be made to unite at very high temperatures, such as that of the electric arc. If the two carbon poles of a powerful battery or dynamo are enclosed in a vessel filled with hydrogen, and a strong electric current passed from pole to pole, acetylene is formed. It is a colourless gas possessing a peculiar and disagreeable smell; it burns with a smoky luminous flame when a light is brought in contact with it. Acetylene is also formed in cases where the combustion is incomplete, as when, for instance, the Bunsen burner "burns down," that is, when the coal-gas burns from the jet at the bottom of the tube instead of the mixture of air and gas burning at the top (see p. 236).

EXPT. 133.—To show the formation of this gas, place a glass tube 12 inches long over the Bunsen when burning down, and invert over this tube a large flask, the inner surface of which has been moistened with an ammoniacal solution of cuprous chloride.* The blue colour of this solution will in a few moments be changed to a deep red, owing to the formation of a red insoluble compound of acetylene with cuprous oxide. This is an excellent test for the presence of this compound. Acetylene combines directly with hydrogen to form the next compound, ethylene, $C_2H_2 + H_2 = C_2H_4$.

Ethylene or Oleflant Gas

FORMULA C_2H_4. MOLECULAR WEIGHT 27.8. DENSITY 13.9

This gas is one of the chief constituents of the product of the destructive distillation of coal (see coal-gas, p. 234), and it is chiefly to its presence that coal-gas owes its luminous qualities.

Preparation.—In order to prepare ethylene in a pure state, 1 part of alcohol or spirits of wine (C_2H_6O) is heated

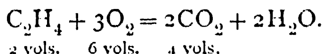
* Cuprous chloride, Cu_2Cl_2, is prepared by the action of metallic copper on a boiling solution of cupric chloride, $CuCl_2$, and hydrochloric acid.

in a flask with 5 or 6 parts of strong sulphuric acid, this mixture being first made by carefully pouring the alcohol into the sulphuric acid in a thin stream, whilst the mixture is constantly stirred. In this experiment the flask should previously be half filled with dry sand and the mixture poured on to it, as otherwise the liquid is apt to froth over. On heating the flask, care being taken that the sand at the bottom of the flask is wetted with the mixture, ethylene gas is quickly evolved and may be collected as usual over water. The reaction that here occurs is similar to that by which carbon monoxide is prepared from formic acid (p. 223); the sulphuric acid removes the element of water (H_2O) from the alcohol and C_2H_4 is evolved.

Properties.—Ethylene is a colourless gas having a sweetish taste; when cooled to $-110°$ it condenses to a colourless liquid which at $-160°$ solidifies. It burns with a brightly luminous flame when a light is applied. To show this best, a cylinder filled with the gas is opened, a lighted taper applied to the mouth, and water quickly poured in, when a large smoky flame issues with formation of carbon dioxide and water.

When mixed with three times its volume of oxygen and fired, the mixture detonates very strongly. Care must be taken in making this experiment. The above mixture may be made in an ordinary glass flask, and the flask then corked and wrapped up in a strong towel, care being taken to leave the mouth of the flask exposed. On removing the cork and bringing a lighted taper to the mouth a violent explosion occurs and the flask is shattered to pieces. Unless the above precautions are taken the glass of the flask is thrown about and serious results might follow.

Two volumes of olefiant gas, C_2H_4, require for their complete combustion 6 volumes of oxygen; 4 volumes for C_2, forming 4 volumes of CO_2, and 2 for the hydrogen, forming 4 volumes of water as shown in the equation.



$$\underset{2\text{ vols.}}{C_2H_4} + \underset{6\text{ vols.}}{3O_2} = \underset{4\text{ vols.}}{2CO_2} + 2H_2O.$$

Ethylene derives its old name, olefiant, or oil-making, gas from the fact that it unites with its own volume of chlorine to form an oily liquid, $C_2H_4Cl_2$, ethylene dichloride.

Coal-Gas and Flame

This substance, manufactured on so large a scale for illuminating and heating purposes, is not a chemical compound but a mixture of many compounds. If bituminous coal be heated to redness in a closed retort three distinct kinds of products are given off: (1) gas tar; (2) ammonia liquor or gas water; and (3) gas. Tar is a mixture of a great variety of chemical compounds, many of which now yield very valuable products, such as the aniline colours, besides scents and useful medicines. The ammonia liquor is the chief source of the ammoniacal salts; it is derived from the nitrogen which the coal contains. The gas contains several ingredients, some of which are harmful and must be removed, whilst others are useful and must be retained. Amongst the former are carbon dioxide (CO_2), sulphuretted hydrogen (SH_2), and the vapour of carbon disulphide (CS_2), and these impurities are more or less completely removed from the gas before it is sent out from the gasworks for consumption. The useful ingredients may be divided into two classes: (1) those which act as illuminating agents; and (2) those which burn and give out heat, but do not give off light when burning. The first class consists chiefly of ethylene, mixed with small quantities of acetylene, C_2H_2, and the vapours and other hydrocarbons such as propylene (C_3H_6) and benzene (C_6H_6); in the second class are contained hydrogen, carbonic oxide, and methane or marsh gas (CH_4), these serve as diluents to dilute the ethylene, which by itself burns with too smoky a flame to be available for ordinary purposes. Various kinds of coal yield gas which differs both in composition and in illuminating power; moreover the heat to which the coal is subjected greatly affects the properties and composition of the gas evolved.

The degree of luminosity of coal-gas is ascertained by comparison with the light given out by a standard candle. Of course the size of the flame, or the rate at which the gas is burning, must be taken into account. For this purpose the standard used is a flame consuming 5 cubic feet of gas per hour. When a coal-gas is said to be equal to 17.5 candles, this means that a gas flame burning at the above rate gives off an

amount of light 17.5 times as great as that of one standard candle.

Water-gas is a mixture of hydrogen and carbon monoxide obtained by passing steam over red-hot coal or coke, when the following decomposition occurs—



$$C + H_2O = CO + H_2.$$

This gas burns with a non-luminous but very hot flame, and it is therefore used for steel-making and for other purposes where a high temperature is needed. For illuminating purposes the flame is allowed to impinge on a comb of magnesia, which becomes white hot, and then emits a powerful light.

The Structure of Flame

Flame is gas in a highly-heated or incandescent state. If flame passes quickly through an inflammable mixture, such as oxygen and hydrogen, or coal-gas and air, or if a rapid combustion of a solid or liquid body, such as gunpowder or nitroglycerine, takes place, the sudden expansion gives rise to an explosion. If, however, the inflammable gases come slowly into contact with the air, as in the case of a jet of coal-gas, or of a lighted lamp or candle, a steady flame is seen. A candle flame consists of three parts or zones—(1) the dark central zone consisting of the supply of combustible and unburnt gas surrounding the wick; (2) the luminous zones; (3) the non-luminous exterior zone.

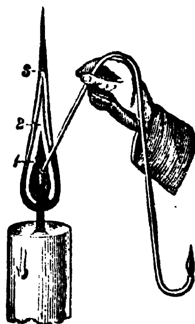


Fig. 104.

EXPT. 134.—By bringing the end of the bent tube (Fig. 104) into the interior zone the unburnt gases may easily be withdrawn from the centre of the flame, and lighted at the longer end of the syphon-tube. In the luminous zone the combustion is incomplete, and carbon in the form of soot is separated out. This is easily shown by holding a card or sheet of stiff paper horizontally in the candle flame for a few moments, so as not to burn the paper, when on withdrawing the card a black

ring of soot is seen to be deposited, whilst the centre remains white. The luminosity of a flame depends on the presence of solid particles; where the combustion is complete, that is, where all the carbon is at once burnt up to carbon dioxide as in the outer zone (3) of the candle flame, no luminosity occurs, but if we bring a thin piece of platinum wire into this part of the flame, we see that the wire becomes white hot, and gives off light. The effect of complete combustion rendering the flame non-luminous is seen in the Bunsen burner, now generally used in laboratories. Its construction is seen in Fig. 105; the coal-gas issues from a small burner (*a*) at the foot of the lamp, and passes up unburnt to the top of the tube (*e*), where it mixes with air drawn up the tube through the holes (*dd*); on bringing a light to the top of the tube, the mixture of air and gas burns with a blue, perfectly smokeless flame; but if the holes (*dd*) are closed by the fingers, the gas burns with the ordinary luminous flame. This non-luminous flame, like a candle flame, is hollow. To show this, several experiments can be made.

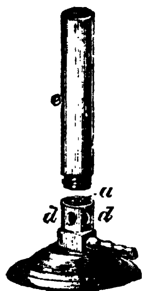


Fig. 105.

EXPT. 135.—Take a thin platinum wire, and hold it horizontally in the Bunsen flame. It will then be noticed that the wire becomes brightly luminous in two points at each side of the flame, whilst the part of the wire in the centre of the flame does not glow. Again, thrust the head of a lucifer match quickly through a Bunsen flame to the centre, when it will be seen that the tip may be held for some time in the central zone without taking fire, whilst the wood will be charred where it comes in contact with the heated outer mantle.

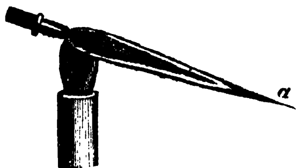


Fig. 106.

EXPT. 136. **The Blowpipe Flame.** — Place a hollow tube, having the upper end flattened and sloped, inside the tube of the Bunsen, so that the air is prevented from entering the holes (*dd*, Fig. 105), and then urge the luminous flame with a mouth blowpipe. It will be seen that, like the candle flame, that of the blowpipe consists of two parts—(1) the oxidising or outer

part of the flame (*a*); and (2) the reducing or inner part (*b*). In the first there is an excess of oxygen, and the flame is non-luminous; in the second there is an excess of carbon, and the flame is luminous. To show the different effects which these two parts of the flame exert, let us make a colourless borax bead on a loop of platinum wire, by heating a little powdered borax on the loop until it fuses to a colourless glass. Then dip this bead into a solution of ferric chloride (Fe_2Cl_6); on heating the bead in the outer flame it will be seen that the borax-glass becomes coloured yellow; next heat it carefully in the inner or reducing flame, and it will be seen that the colour of the bead is changed to green. This is due to the reduction of the ferric oxide, Fe_2O_3 (formed in the outer flame), to ferrous oxide, FeO, in the inner flame.

The Davy Lamp.—In order that a gas shall become ignited, the temperature of the gas must be raised to a certain point; below this point the gas will not inflame. Different gases and vapours ignite at very different temperatures.

EXPT. 137.—To show this, try to light a jet of coal-gas with a red-hot splinter of wood. You will not succeed in doing this, but blow the red-hot splinter into a flame, and the gas at once ignites. Then pour a few drops of bisulphide of carbon (CS_2) into a saucer and try the same experiment. The red-hot splinter of wood immediately ignites the vapour, which then burns with a lambent-blue flame with evolution of $SO_2 + CO_2$.

A candle flame may be so cooled down as to extinguish it. For this purpose make a coil of cold copper wire, and place it over the flame; the flame will at once go out. Then heat the coil and repeat the experiment, when the flame will continue to burn.

It is upon this principle that the "Davy" or safety-lamp for coal-miners is constructed. To understand this, let us make a simple experiment. Take a square piece of wire gauze, containing about 700 meshes to the square inch. Hold this over a jet of gas, and light the gas on the top of the gauze; then carefully raise the gauze, and observe that whilst the flame continues to burn on the upper surface, the

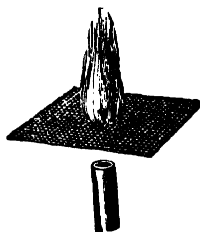


Fig. 107.

flame is seen not to pass through the gauze, and no flame exists below it. The metal wires here so quickly conduct away the heat of the flame that the temperature of the inflammable gas below the gauze never reaches the point of ignition, and the gauze may be moved upwards so that at last the flame is extinguished, although the gas continues to escape from the jet. Now imagine this gauze wrapped round a lighted candle, both above, below, and at the sides. The air can get through the meshes, and the products of the combustion can escape, but if you approach the outer side of the gauze with an unlighted jet of gas, you will not be able to light the jet. This is the "Davy Lamp." Its construction is seen in Fig. 108. A gauze cover is screwed on to the rim of an oil lamp, and when the lamp is lighted, and the cover screwed on, it may be plunged into a large beaker, at the bottom of which a small quantity of ether has been poured, and yet the inflammable vapour of the ether will not become ignited. Then remove the safety-lamp, and throw into the beaker a bit of burning paper, and the whole vessel will at once be filled with flame. This experiment illustrates the use of this lamp in coal-pits where inflammable mixtures of "fire-damp" and air are liable to occur.

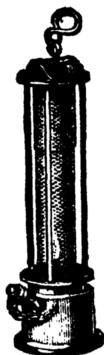


Fig. 108.

What we have learnt

In our twenty-first Lesson we have studied the various allotropic forms of carbon, viz. diamond, graphite, and charcoal in its various forms. Carbon monoxide is prepared by the action of strong sulphuric acid on formic acid or oxalic acid, in the latter case the CO is mixed with an equal volume of CO_2. Carbon monoxide is also produced when charcoal is burnt in an insufficient supply of air, or when carbon dioxide is passed over red-hot charcoal. CO is a colourless poisonous gas, which burns in the air with a lambent blue flame forming CO_2. Its composition may be determined by exploding it with oxygen in a eudiometer, when it is found that 2 volumes of CO (density 13.9) combine with 1 volume of oxygen to form 2 volumes of CO_2.

Carbon dioxide is prepared by the action of hydrochloric acid on marble, or it is produced whenever carbon or carbon compounds burn in excess of air. It is slightly soluble in water, the amount dissolved being proportional to the pressure at which solution is effected. It exists dissolved under pres-

sure in all effervescent beverages, and, although sometimes introduced artificially, it is produced naturally in other cases by a process of fermentation. CO_2 is a very heavy gas, and may be collected by downward displacement. Its composition is ascertained by the same method as was used for sulphur dioxide.

CO_2 is recognised by its power of rendering lime-water turbid. It is the anhydride of carbonic acid, H_2CO_3, which, like sulphurous and sulphuric acids, is dibasic, and forms therefore two series of salts, viz. M'_2CO_3 and $M'HCO_3$.

The hydrocarbons marsh gas, CH_4, acetylene, C_2H_2, and ethylene, C_2H_4, have been shortly considered, as also has coal gas, which is a mixture of various gases obtained by the destructive distillation of coal. Finally, we have studied the structure of flame, and its chemical characters. We have seen how a knowledge of the characters of flame, and the conditions under which it is produced, led Sir Humphry Davy to devise the safety-lamp for miners.

Exercises on Lesson XXI

1. By what three methods could you prepare carbon monoxide?

2. What are the properties of carbon monoxide and dioxide, and how may their composition be determined?

3. How would you distinguish carbon monoxide from hydrogen and from marsh gas?

4. How would you prepare marsh gas and ethylene?

5. Why is it that miners often perish in a coal mine after an explosion of fire-damp, although unhurt by the actual explosion?

6. Describe the eudiometric analysis of marsh gas, giving the volume ratios.

7. Explain the burning of a candle.

8. By what experiments would you illustrate the principle of the Davy safety-lamp?

9. What volume of CO_2 at NTP can be obtained from 185 grams of marble (1) by decomposing it by heat; (2) by acting on it by dilute nitric acid?

10. By what tests would you recognise that a certain gas is a compound of carbon and hydrogen?

11. What is *water gas*? Give an equation showing its formation. What are the products of its combustion in (1) air, (2) oxygen?

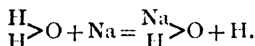
12. How is bicarbonate of soda prepared? What happens when CO_2 is passed through lime-water (1) in small quantity, (2) in large quantity, and what happens in the last case when the liquid is boiled?

APPENDIX

I.—EQUIVALENTS AND ATOMIC WEIGHTS

Methods of Determining Equivalents.—On pages 27, 28, and 32 we have learnt the meaning of the term "*chemical equivalent.*"

There are very many ways of ascertaining the equivalent of an element. On p. 32 we found the equivalent of sodium by the direct replacement of hydrogen by the metal



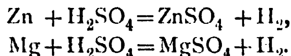
$$\begin{matrix}H\\H\end{matrix}>O + Na = \begin{matrix}Na\\H\end{matrix}>O + H.$$

Here we have only to ascertain experimentally what weight of sodium *takes the place of one part by weight of hydrogen.*

If we gradually add 22.9 grams of sodium to water and carefully collect the hydrogen which is evolved, it is found to occupy 11.125 litres [at NTP]; and we have learnt (p. 56) that this volume of hydrogen weighs exactly *one gram.*

Therefore 22.9 grams of sodium are equivalent to 1 gram of hydrogen, and the "*equivalent*" of sodium is therefore 22.9.

The equivalents of all metals which displace hydrogen from water or acids may be found in the same manner, *e.g.*—



$$Zn + H_2SO_4 = ZnSO_4 + H_2,$$
$$Mg + H_2SO_4 = MgSO_4 + H_2.$$

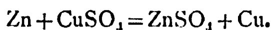
Another method by which the equivalent of an element may be obtained is by the accurate analysis of a compound of that element with hydrogen, if such exists.

That weight of an element which combines with *one part by weight of hydrogen* represents the equivalent.

But suppose we wish to find the equivalent of an element which does not displace hydrogen from water or acids, like sodium and zinc, nor yet forms a compound with hydrogen.

In many cases of this kind, *e.g.* copper, the equivalent of one element being known as compared with hydrogen, it is easy to find the equivalent of another, by the direct displacement of one metal by another in one of its soluble salts, *e.g.*—

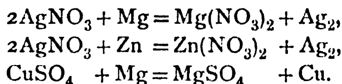
When metallic zinc (or iron, see Expt. 17, p. 23) is placed in a solution of copper sulphate, the zinc dissolves and becomes zinc sulphate, whilst the copper is deposited in the metallic state.



$$Zn + CuSO_4 = ZnSO_4 + Cu.$$

All we have to do, therefore, is to weigh a piece of thin sheet zinc and place it in a solution of copper sulphate until all the zinc has become dissolved and then accurately weigh the pure copper which has been deposited. Then we can easily calculate the weight of copper which is equal in combining power to the *equivalent* weight of zinc, and the weight we thus find is the equivalent of copper.

The same method may be applied in other cases, *e.g.*—

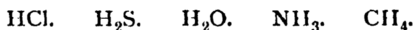


$$2AgNO_3 + Mg = Mg(NO_3)_2 + Ag_2,$$
$$2AgNO_3 + Zn = Zn(NO_3)_2 + Ag_2,$$
$$CuSO_4 + Mg = MgSO_4 + Cu.$$

The same end may be attained by the electro-deposition of metals. It is found that if *the same current* is passed through two electrolytic cells in which different metals are deposited in the metallic state, then the weights deposited are in the ratio of their equivalents. If one of the cells contains acidulated water whilst the other contains copper sulphate, then the weight of hydrogen liberated at the negative pole in one cell (p. 15) will be *one gram*, when the weight of copper deposited in the other amounts to 31.4 grams. This number being the equivalent of copper. The equivalent of copper determined by this latter method agrees with that found by precipitation with zinc described above.

Indeed there are very many ways in which equivalents may be determined experimentally, such as, *e.g.* the accurate gravimetric analysis of chlorides, sulphates, nitrates, oxides, etc.

Relation between Equivalents and Atomic Weights.—In the foregoing Lessons we have learnt that the following formulæ represent the molecules of the several substances for which they stand, viz.—



$$HCl. \quad H_2S. \quad H_2O. \quad NH_3. \quad CH_4.$$

Assuming for the moment that these formulæ are correct, we notice that chlorine combines with hydrogen atom for atom, whilst the atoms of sulphur and oxygen each combine with two atoms of hydrogen, whilst the atoms of nitrogen and carbon combine with three and four atoms of hydrogen respectively.

Remembering that the equivalent of an element is always compared with one part by weight of hydrogen (one atom), we notice that in the case of chlorine, the *atomic* and *equivalent* weights for that element are identical.

In the cases of sulphur and oxygen, the atomic weight represents *twice* the equivalent; whilst in the cases of nitrogen and carbon, the atomic weights of those elements represent three and four times the equivalent respectively.

It is thus evident that *the atomic weight of an element is always either identical with or is some simple multiple of the equivalent of that element.*

We learn also that the atomic weight of an element is represented by the equivalent multiplied by the *valency* (p. 82) of that element, chlorine being monovalent, sulphur and oxygen being divalent, and nitrogen and carbon trivalent and tetravalent respectively.

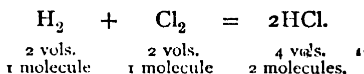
Avogadro's Law and Molecular Weights, Determination of Atomic Weights.—We have learnt on p. 59 that equal volumes of all gases contain the same number of molecules. This is known as Avogadro's law, which is accepted as true both by chemists and physicists.

It follows from this law that *the molecular weights of all gases are proportional to their densities*, for, since equal volumes of all gases contain the same *number* of molecules, the weights of a standard volume of all gases will be proportional to the weight of the individual molecules of each different gas.

This law, however, does not tell us directly how many atoms are contained in the molecule of any particular gas. We will now consider how, in certain cases, it may be made to do so indirectly.

We have learnt on p. 55 that the molecules of the elementary gases consist, with a few exceptions, of *two* atoms. The following reasoning will show how this conclusion has been arrived at.

We know from Experiments 101-106, pp. 179-183, that equal volumes of hydrogen and chlorine combine together, *without change of volume*, to form hydrochloric acid gas. Let us erroneously assume that the molecules of hydrogen and chlorine consist of single atoms in each case. Then after combination to form molecules of HCl there will be just half the original number of molecules, two molecules having joined together to form a single molecule of two atoms. Now according to Avogadro's law the volume of the product should in this case be half the total volume of its separate constituents. This is not the case; therefore the above supposition is erroneous. We must conclude, therefore, that the molecules of hydrogen and chlorine consist of two atoms in each case, and there are good reasons for knowing that they do not consist of more than two atoms. Then our observed fact becomes accordant with Avogadro's law as the following equation shows—



$$H_2 \quad + \quad Cl_2 \quad = \quad 2HCl.$$

2 vols. 2 vols. 4 vols.
1 molecule 1 molecule 2 molecules.

We must also conclude that an atom of chlorine is combined with an atom of hydrogen in every molecule of hydrochloric acid gas. The equivalent of chlorine is 35.2, this weight combines with one part by weight of hydrogen. It also represents an atom, therefore 35.2 is the atomic weight of chlorine and is identical with its equivalent.

Accepting, then, as true that a molecule of hydrogen is composed of *two* atoms, each weighing unity, the molecule of this gas must weigh *two*, and since the density of hydrogen is taken as unity, the molecular weight of hydrogen is twice the density.

Now since the molecular weight of hydrogen is taken as twice the density, the molecular weight of any other gas must *also* be taken as twice its density, since densities are proportional to molecular weights, according to the deduction we have already made from Avogadro's law.

Evidently, then, knowing experimentally the density of any gas, we have the means of finding the *molecular weight* of that gas relatively to the atom of hydrogen, which is taken as the standard for all atomic weights,[1] for we have only to multiply the density (compared with hydrogen) by two.

This law is now one of the most firmly established laws in chemistry, and is constantly being used as a means of determining molecular weights.

Remembering that the *atom* may be defined as the smallest particle of an element which can form part of a molecule, we are able to obtain confirmation of the truth of the atomic weight of chlorine deduced above. It is found that in a large series of compounds containing chlorine, whose vapour densities and percentage compositions have been determined, no molecule has been found to contain *less than* 35.2 parts by weight of chlorine, though many contain a simple multiple of 35.2 parts, *i.e.* in those cases in which the molecule contains two or more atoms of that element.

We may therefore also define *the atomic weight of an element* as *the smallest weight of that element which can form part of a molecule.*

So long as there is no other evidence to guide us in fixing an atomic weight, this definition gives us a very good method of determining atomic weights. *E.g.* the molecular weights of a large number of carbon compounds have been determined from their densities, and on calculating from their percentage compositions, no molecule has been

[1] We do not know the *absolute* weights of the atoms, but only their *relative* weights, and the atom of hydrogen is taken as the standard with which all other atoms are compared, and its value is taken as unity.

found which contains *less than* 11.9 parts by weight of carbon, and in all cases in which more than 11.9 parts have been found, the weight has been a simple multiple of 11.9 (according to the number of carbon atoms contained in the molecule). Therefore we are justified in accepting 11.9 as the atomic weight, because it is the smallest weight of carbon which can form part of a molecule.

Methods of Control in Determining Atomic Weights. Dulong and Petit's Law.—After a large number of atomic weights had been determined, Dulong and Petit discovered the law relating the specific heat of elements with their atomic weights (see p. 112). This gives us a means of deciding in very many cases whether the equivalent or some simple multiple of it must be taken as the atomic weight of an element.

Let us take the case of silver. We know that 35.2 parts of chlorine combine with 107.1 parts of silver, but this does not tell us whether the 107.1 parts of silver represent one, or more, atoms of that element.

The specific heat of silver has been determined, and has been multiplied by the equivalent, the product being not far removed from 6.3. Therefore the equivalent and atomic weights are identical.

There are many other means of control at the command of the chemist, but these cannot be entered into here, as to discuss them would be beyond the scope of this book.

II. METALS AS DISTINGUISHED FROM NON-METALS—GENERAL CHARACTERS OF METALS—THE METALS OF THE ALKALIS AND ALKALINE EARTHS—LIGHT AND HEAVY METALS

We have seen (pp. 22 and 32) that the elements are divided into two classes, viz. metals and non-metals, and we will now consider in what respects the elements of one class differ from those of the other.

On p. 22 a list is given containing a few of the metals with which nearly every one is familiar, whilst the list on p. 32 contains the names of other metals which are rarely heard of except in the study of chemistry. There are still other metals which are even more rare, and these are left out of consideration altogether in this book, and for an account of them a larger work must be consulted.

This division of metals from non-metals is not a very satisfactory one, because when we begin to try to define a metal we see that there is no real hard and fast line between the properties of the metals and non-metals.

Metals are usually possessed of most of the following properties. They are *elements* which are heavy, *i.e.* have a high specific gravity, hard, opaque, solid at ordinary temperatures, they have a peculiar "metallic" lustre when polished; they are malleable, that is, can be hammered out into thin sheets; they are ductile, *i.e.* can be drawn out into thin wire, they are usually good conductors of heat and electricity.

Their oxides and hydroxides are usually basic, and combine with acids to form salts (see p. 81).

Some of the metals, however, do not possess all these properties, whilst some of the non-metals possess certain properties which we have just mentioned as being characteristic of the metals, *e.g.*

Solidity.—There is one exception to the rule that metals are solid bodies at the ordinary temperature, that is the metal mercury. This is a liquid at ordinary temperatures, but if exposed to great cold (its freezing point is $-40°$ C.) it becomes solid and can then be hammered out, *i.e.* possesses malleability, and can be cut with a knife like a piece of lead.

Heaviness (Specific Gravity, p. 113).—The metals are usually *heavy* solid bodies, yet there are important exceptions. The metals sodium, potassium, and lithium, are lighter than water. These metals (together with rubidium and cæsium) are classed together in one group called the metals of the alkalis, and this group together with the next group comprising calcium, strontium and barium (which are known as the metals of the alkaline earths) are often distinguished as the "light metals," all the rest being grouped together as the "heavy metals."

Gold has a specific gravity of 19.3, that is, gold is more than nineteen times as heavy as water. Platinum has a specific gravity of 21.5, and iridium of 22.5.

The heavy metals are themselves divided into several sub-groups but we need not consider them here.

Hardness.—Not all metals are hard. The metals sodium, potassium, and lead, are comparatively soft, whilst amongst the non-metals we have the diamond (crystallised carbon) which is the hardest substance known.

Opacity.—The metals gold and silver form exceptions, when in sufficiently thin films these metals are transparent, gold transmits green and silver blue light.

Metallic Lustre.—This property of metals is seen when the surface of the metal is polished or cut; metals in a state of fine powder are often gray or black and do not show metallic lustre until they are rubbed to a smooth surface. Some of the non-metals possess a lustre resembling that of the metals, *e.g.* iodine, graphite (carbon), arsenic, tellurium.

Malleability and Ductility.—These properties belong almost exclusively to the metals, but amongst the metals themselves there are some exceptions, *e.g.* bismuth and antimony which are brittle and cannot be hammered without breaking to pieces.

Conductivity for Heat and Electricity.—The metals themselves vary greatly in their electrical conductivity. Silver, being the best conductor of all, has a standard conductivity of 100, whilst mercury has only a conductivity of 1.6, and bismuth 1.2. Graphite amongst the non-metals possesses a marked power of conducting electricity. It is thus evident that the physical properties of the elements alone cannot be altogether relied upon to afford a distinction between metals and non-metals, and we have to rely mainly on the chemical properties and relationships which each element exhibits; and in those cases where the physical properties of the element leave us in doubt as to whether an element should be classed as a metal or non-metal, the chemical characters and relationships are usually sufficiently well marked to decide the question.

The Oxides of metals (and especially the lower oxides) are almost invariably *basic* oxides (see p. 81), whilst the oxides of non-metals are almost invariably *acid-forming* oxides or else possess neither property.

The higher oxides, however, of certain metals, act sometimes as acids to a powerful base, *e.g.* Al_2O_3 which forms sodium aluminate with Na_2O, and SnO_2 which forms sodium stannate with the same base.

Towards powerful acids these same oxides act as bases. With hydrochloric acid they form chlorides, *e.g.* Al_2Cl_6 and $SnCl_4$.

III

By Act of Parliament (27 *and* 28 *Vict. cap.* 117, 29*th July* 1864), *the use of the Metrical System of Weights and Measures is rendered legal. The Weight of the Kilogram is settled by this Act to be equal to* 15432.3487 *English grains.*

COMPARISON OF THE METRICAL WITH THE COMMON MEASURES. BY DR. WARREN DE LA RUE.

MEASURES OF LENGTH.

	In English Inches.	In English Feet =12 Inches.	In English Yards =3 Feet.	In English Fathoms=6 Feet.	In English Miles =1,760 Yards.
Millimetre	0.03937	0.0032809	0.0010936	0.0005468	0.0000006
Centimetre	0.39371	0.0328090	0.0109363	0.0054682	0.0000062
Decimetre	3.93708	0.3280899	0.1093633	0.0546816	0.0000621
Metre	39.37079	3.2808992	1.0936331	0.5468165	0.0006214
Decametre	393.70790	32.8089920	10.9363310	5.4681655	0.0062138
Hectometre	3937.07900	328.0899200	109.3633100	54.6816550	0.0621382
Kilometre	39370.79000	3280.8992000	1093.6331000	546.8165500	0.6213824
Myriometre	393707.90000	32808.9920000	10936.3310000	5468.1655000	6.2138244

1 inch = 2.539944 centimetres.
1 foot = 3.0479449 decimetres.

1 yard = 0.91438348 metre.
1 mile = 1.6093140 kilometres.

MEASURES OF SURFACE.

	In English Sq. Feet.	In English Sq. Yards =9 Sq. Feet.	In English Poles =272.25 Sq. Feet.	In English Roods =10,890 Sq. Feet.	In English Acres =43,560 Sq. Feet.
Centiare or square metre . .	10.7642993	1.1960333	0.0395383	0.000988457	0.0002471143
Are or 100 square metres . .	1076.4299342	119.6033260	3.9538290	0.098845724	0.0247114310
Hectare or 10,000 square metres	107642.9934183	11960.3326020	395.3828959	9.884572398	2.4711430996

1 square inch = 6.4515669 square centimetres.
1 square foot = 9.2899683 square decimetres.

1 square yard = 0.83609715 square metre or centiare.
1 acre = 0.404671021 hectare.

MEASURES OF CAPACITY.

	In Cubic Inches.	In Cubic Feet =1.728 Cubic Inches.	In Pints =34.65923 Cubic Inches.	In Gallons = 8 Pints=277.27384 Cubic Inches.	In Bushels =8 Gallons =2218.19075 Cubic Inches.
Millilitre or cubic centimetre	0.061027	0.0000353	0.001761	0.00022010	0.000027512
Centilitre or 10 cubic centimetres	0.610271	0.0003532	0.017608	0.00220097	0.000275121
Decilitre or 100 cubic centimetres	6.102705	0.0035317	0.176077	0.02200967	0.002751208
Litre or cubic decimetre	61.027052	0.0353166	1.760773	0.22009668	0.027512085
Decalitre or centistere	610.270515	0.3531658	17.607734	2.20096677	0.275120846
Hectolitre or decistere	6102.705152	3.5316581	176.077341	22.00966767	2.751208459
Kilolitre or stere, or cubic metre	61027.051519	35.3165807	1760.773414	220.09667675	27.512084594
Myriolitre or decastere	610270.515194	353.1658074	17607.734140	2200.96676750	275.120845937

1 cubic inch = 16.3861759 cubic centimetres. 1 cubic foot = 28.3153119 cubic decimetres.
1 gallon = 4.543457969 litres.

MEASURES OF WEIGHT.

	In English Grains.	In Troy Ounces =480 Grains.	In Avoirdupois Lbs. =7,000 Grains.	In Cwts. =112 Lbs. =734.000 Grains.	In Tons=20 Cwt. =15,620,000 Grains.
Milligram	0.015432	0.000032	0.0000022	0.00000002	0.000000001
Centigram	0.154323	0.000322	0.0000220	0.00000020	0.000000010
Decigram	1.543235	0.003215	0.0002205	0.00000197	0.000000098
Gram	15.432349	0.032151	0.0022046	0.00001968	0.000000984
Decagram	154.323488	0.321507	0.0220462	0.00019684	0.000009842
Hectogram	1543.234880	3.215073	0.2204621	0.00196841	0.000098421
Kilogram	15432.348800	32.150727	2.2046213	0.01968412	0.000984206
Myriogram	154323.488000	321.507267	22.0462126	0.19684118	0.009842059

1 grain = 0.06479895 gram. 1 lb. avd. = 0.45359265 kilogr.
1 troy oz. = 31.103496 grams. 1 cwt. = 50.80237689 kilogr.

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